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CATALYTIC REDUCTION OF  
CARBON MONOXIDE  
WITH HYDROGEN

*by S. D. Rosenberg, G. A. Guter,  
F. E. Miller, and G. R. Jameson*

Prepared under Contract No. NAS 7-225 by  
AEROJET-GENERAL CORPORATION  
Azusa, California

for

# CATALYTIC REDUCTION OF CARBON MONOXIDE

## WITH HYDROGEN

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## I. OBJECTIVE

The objective of this program was to study the reaction of carbon monoxide and hydrogen, under a variety of conditions, to yield water and a carbon-containing material, preferably methane. Sufficient data was to be obtained to permit a preliminary evaluation of this reaction as a step in the reduction of silicate materials (lunar raw material) to produce oxygen.

## II. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

### A. SUMMARY

#### 1. Task 1, Design

Task 1 was devoted to the design of bench-scale equipment for use in determining the feasibility of the first and second steps in the Aerojet carbothermal process for the manufacture of oxygen from lunar minerals.

a. A small reactor (10 scfh of reactant gas) for the reduction of carbon monoxide with hydrogen was designed. Maximum flexibility of operation was stressed to provide the ability to operate at temperatures of 200 to 900°C, at pressures of 1 to 7 atm, and at hydrogen/carbon monoxide mole ratios ranging from 1:1 to 4:1.

b. A small reactor (50 cc rock capacity) was designed for the reduction of natural silicate rock with methane. A 10 kva induction furnace will be utilized to provide reaction temperatures up to 2200°C.

#### 2. Task 2, Fabrication

Task 2 was devoted to the construction of the bench-scale equipment for the study of the second step of the process (i.e., the reduction of carbon monoxide with hydrogen). The catalyst chamber was fabricated from a

Type 316 stainless steel fin-tube in order to withstand the high temperatures and high heat fluxes required. Standard industrial and laboratory equipment were used wherever possible in order to simplify and speed construction.

### 3. Task 3, Testing

This task was devoted to proving that the test equipment would perform according to design. Tests were made which demonstrated that the equipment can be operated successfully at temperatures from 200 to 900°C, and at pressures from 1.0 to 7.0 atm. The temperatures of the three catalyst bed sections were controllable to  $\pm 2^\circ\text{C}$  with a differential of  $\pm 200^\circ\text{C}$ . An initial charge of catalyst was successfully reduced and activated by flowing hydrogen through it at temperatures up to 450°C for 5 hours. Three preliminary runs demonstrated that the equipment was capable of yielding excellent data for the intended research.

### 4. Task 4, Data Acquisition

Task 4 was devoted to obtaining data on the reduction of carbon monoxide with hydrogen. Three different catalysts were evaluated. In addition, a series of runs was made to determine (a) how various impurities in the reactant gas affect catalyst activity, and (b) the feasibility of accomplishing the reduction without a catalyst.

#### a. Catalyst C-0765-1005

A series of 26 successful data-producing runs was made with Catalyst C-0765-1005 (25% Ni on 4 to 8 mesh silica gel). Optimum operating conditions for this catalyst were found to be as follows: space velocity, approximately  $1000\text{ hr}^{-1}$ ; hydrogen/carbon monoxide mole ratio, 4:1; catalyst bed pressure, 6 atm; and catalyst bed temperature, approximately 425°C. Under these conditions, carbon monoxide conversions were greater than 99.8%, yields of water and methane were greater than 99%, and yields of carbon dioxide were less than 1%. No other hydrocarbons or oxygenated compounds were found in either the product water or gases. Less than 0.1% of the carbon monoxide was deposited on the catalyst as carbon.

b. Catalyst C-0765-1001

A series of 12 data-producing runs was made with Catalyst C-0765-1001 (50% Ni on kieselguhr, 1/8-in.-dia pellets). This catalyst was greatly superior to Catalyst C-0765-1005. Nearly complete conversions were obtained under the following conditions: space velocities of  $2000 \text{ hr}^{-1}$ ; hydrogen/carbon monoxide mole ratio of 4:1; atmospheric pressure; and a reaction temperature of only  $250^{\circ}\text{C}$ . The hydrogen/carbon monoxide mole ratio could be reduced to 3:1 at 6.1 atm,  $1000 \text{ hr}^{-1}$  space velocity, and  $250^{\circ}\text{C}$  while still maintaining nearly complete conversions ( $\text{CH}_4$  and  $\text{H}_2\text{O}$  yields of 99%+,  $\text{CO}_2$  yield of less than 1%). At the 3:1 hydrogen/carbon monoxide mole ratio, the product gas contained more than 90% methane and less than 0.5% carbon dioxide.

Pressure drop across the catalyst was low (less than 1 in. of water  $\Delta P$  with  $1000 \text{ hr}^{-1}$  space velocity and 6.1 atm). The pressure drop did not build up with time, and no carbon was found deposited on the catalyst. The catalyst was still active when it was removed after 110 hours of operation. A deep (38.5 in.) catalyst bed was required to obtain nearly complete conversion of the carbon dioxide (produced in the top of the catalyst bed) when the low hydrogen/carbon monoxide mole ratio was used.

c. Catalyst C-0765-1003

This catalyst, which contained about 15% nickel deposited on kieselguhr (5/32-in. extruded pellets), was found to be intermediate in activity between the first two catalysts tested. The catalyst was not active at  $250^{\circ}\text{C}$ , but was quite active at  $350^{\circ}\text{C}$ . Increasing the catalyst bed temperature to  $400^{\circ}\text{C}$  did not increase the conversion of carbon dioxide into methane and water at a hydrogen/carbon monoxide mole ratio of 3:1.

d. Bare Tube

A series of four runs was made without catalyst (bare tube) in the reactor. These runs were made under the following conditions: space velocity of  $550 \text{ hr}^{-1}$ ; pressure of 6.1 atm; hydrogen/carbon monoxide mole ratio of 3.7:1; and temperatures of 500 to  $900^{\circ}\text{C}$ . The data show that the maximum carbon monoxide conversion was only about 44% at  $700^{\circ}\text{C}$ ; about 15 to 25% of the conversion was to carbon dioxide rather than to methane and water.



e. Impurities

Three series of runs were made with the best catalyst (C-0765-1001) in which impurities were purposely added to the reactant hydrogen gas. A run of 22 hours duration was made with 59 grains of sulfur/100 scf (as COS) in the hydrogen stream. In this time more than 3 g of sulfur (equivalent to 3.9 wt% of the nickel in the catalyst) was charged to the reactor. Although the top third of the reactor had absorbed nearly all of the sulfur and was nearly deactivated, the remaining two-thirds of the reactor continued to operate with only a small decrease in conversion and yields.

A run of 10 hours duration with 1 vol% nitrogen oxide (NO) in the hydrogen reactant gas demonstrated that this nitrogen oxide does not damage the catalyst. However, the oxide is reduced (75 wt% to  $\text{NH}_3$ , 25 wt% to  $\text{N}_2$ ); this ammonia would have to be removed from the product gases and the hydrogen recovered for a lunar process.

A run of less than 3 hours duration with 0.5 mole% phosphine ( $\text{PH}_3$ ) in the hydrogen reactant gas demonstrated that phosphorus is an active catalyst poison which will have to be removed from the reactant gases. Approximately one-half of the catalyst bed was deactivated and its pressure drop increased greatly during the short run.

Carbon dioxide and water in the amounts normally present in the catalyst bed were not found to be harmful. A low concentration of nitrogen (0.5%  $\text{N}_2$ ) present in the carbon monoxide reactant gas did not harm the catalyst.

5. Task 5, Process Integration

This task was devoted to integrating the various steps of the overall process so as to obtain a logical plan of development. The Aerojet carbo-thermal process for the manufacture of oxygen from lunar materials is a three-step process in which hydrogen and methane are continuously recycled, and oxygen and slag are the major products. The first step is the reduction of lunar silicate material with methane to form hydrogen, carbon monoxide, and slag. The second step is the reduction of the carbon monoxide with hydrogen to yield methane for recycle and water. The water is electrolyzed in the third step to yield oxygen (product) and hydrogen for recycle.

The feasibility of the second step has been thoroughly demonstrated in this program; equipment for the first step has been designed on this program and the feasibility of the process will be demonstrated on an extension to the program. The next logical step in the development of the process is integration of Steps 1 and 2 into a continuous process. A flow diagram for such an integrated process was developed.

#### B. CONCLUSIONS

1. The objectives of the program have been achieved. The feasibility of the quantitative reduction of carbon monoxide with hydrogen to form methane and water utilizing a modified Fischer-Tropsch synthesis was unequivocally demonstrated.

2. Reaction conditions were found which yield (a) virtually quantitative conversion of carbon monoxide to methane and water, (b) carbon dioxide in less than 1.0%, (c) negligible carbon formation, (d) methane as the exclusive organic product, and (e) a 90% methane concentration in the product gas.

3. An excellent nickel-containing catalyst was found which achieves these excellent results at low catalyst bed temperature and pressure and high space velocity ( $250^{\circ}\text{C}$ , 1.0 to 6.0 atm, and  $1000\text{ hr}^{-1}$ ).

4. The uncatalyzed reduction of carbon monoxide with hydrogen does not produce sufficiently high yields of methane and water to warrant further consideration. Maximum carbon monoxide conversion was only 44% at  $700^{\circ}\text{C}$  and the yield of carbon dioxide was intolerably high - 15 to 25%.

5. Sulfur and phosphorus compounds must be completely removed from the reactant gases prior to contact with the catalyst bed to obtain suitable catalyst life.

6. The design of a bench-scale reactor to determine the feasibility of the first step of the process (i.e., the reduction of silicate rock with methane to form carbon monoxide and hydrogen) is complete.

### C. RECOMMENDATIONS

The Aerojet carbothermal process has three essential steps: (1) the reduction of silicate with methane to form carbon monoxide and hydrogen; (2) the reduction of carbon monoxide with hydrogen to form methane and water; and (3) the electrolysis of water to form hydrogen and oxygen. The process is cyclic in nature, with the methane and hydrogen returned to the system.

1. The determination of the feasibility of Step 1 of the process should be started promptly.

2. The present program was not able to provide long-term activity data for the candidate catalysts evaluated for use in Step 2. Such data can be obtained only by carrying out the reaction on a continuous basis over prolonged time periods (30 to 90 days). Such a study will also provide information on the more subtle effects of impurities on catalyst activity and product yield, and more precise material balances for reactants and products. The orderly development of the Aerojet carbothermal process requires, therefore, that the carbon monoxide reduction reaction be studied on an increased scale for prolonged time periods, utilizing the reaction data determined on the present program as the basis for reactor design and fabrication. This research should be started promptly.

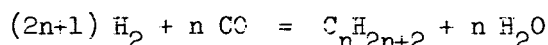
3. The separation of water into its elements is required for many of the chemical cycles which will find use in extraterrestrial applications, including Step 3 of the Aerojet carbothermal process. Electrolysis appears to be the only practical method for the decomposition of water. Commercially available equipment, however, cannot be utilized where light weight is required for payload savings. In addition, electrode efficiency can be improved by judicious choice of electrode materials. The importance of this reaction requires that it be studied promptly.

### III. TECHNICAL DISCUSSION

Research on the first increment of Contract NAS 7-225 was initiated 22 April 1963 and completed 15 November 1963. The program was divided into six tasks: Task 1, Design; Task 2, Fabrication; Task 3, Testing; Task 4, Data Acquisition; Task 5, Process Integration; and Task 6, Reports.

## A. LITERATURE SURVEY

The literature on the reaction of carbon monoxide with hydrogen was studied with care during the program period. Due to the copious amount of work which has been done on the many facets of this reaction and the rapid pace with which the program was required to move, it was necessary to rely heavily on previous literature surveys. Two literature reviews (References 1 and 2) were found to be of particular value as aids in locating the most recent pertinent work. Reference 1 contains a wealth of thermodynamic data for the reactions



and several related reactions producing a variety of other products.

Reference 2 is a bibliography containing 3711 abstracts of papers and 4017 abstracts of patents. These sources were helpful in locating the most recent literature (References 3 through 7) on the reaction to form methane as a primary product. Investigation 5137 of the U.S. Bureau of Mines was very helpful in the design of the equipment and in the choice of the catalysts. This report appeared to be the most recent of significant work on the reaction and is representative of the state of the art before the present program was initiated.

Although much work was devoted to studies by others on the production of methane, such work was directed toward objectives which are considerably different from the objectives of this program. Previous investigators sought a hydrocarbon product of commercial interest and had little regard for water production or precise material balances. Because this investigation was concerned with a reaction intended for use on the lunar surface, water became an important product, and loss of carbon, hydrogen, and oxygen in the reaction was a critical factor to be considered. These broad objectives were borne in mind when the literature was reviewed to select data for design, construction, and operating conditions of the flow apparatus.

## B. TASKS 1 AND 2, DESIGN AND FABRICATION

### 1. Design of the Reactor for the Reduction of Carbon Monoxide with Hydrogen

The equipment used in the study of the reaction of carbon monoxide with hydrogen was designed to allow maximum flexibility in operating conditions. Type 316 stainless steel was chosen as the reaction-chamber metal because of its high temperature strength, resistance to corrosion, and nickel content. The U.S. Bureau of Mines (Reference 3) used carbon steel chambers in its laboratory scale equipment.

Figure 1 is a schematic flow diagram of the hydrogen-carbon monoxide reactor designed for this investigation. Heat dissipation is one of the major problems associated with the reaction as it is highly exothermic. This problem was minimized by making the reaction chamber (1)\* small in diameter (0.527 in. ID) in relation to its length (38.5 in.). This design provided a large surface area for cooling and a minimum distance for the reacting gases to travel from the center of the chamber to the cooling surface. Fins were provided on the outside of the tube to furnish additional cooling surface. For convenience, air was used as the cooling fluid. In a lunar installation, a fluid such as Dowtherm or a molten salt, would be recirculated through an exchanger or radiator to dissipate the heat of reaction.

The reaction chamber was divided into three separate sections for temperature control. Each section was provided with an electrical heating unit (2) and a separate air-cooling system. This provided the unit with capability for adjusting the temperature profile of the reactor as desired.

Commercial grade hydrogen and carbon monoxide from compressed gas cylinders were used in these studies. Two-stage pressure-reducing regulators, needle valves and rotameters, or orifices and manometers, were used to control the flow rates. The pressure on the reactor was controlled by a motor valve (11) which was operated by an automatic pressure recorder and controller (not shown).

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\* Numbers refer to coding system used in Figure 1 to label reactor components.

Electric heaters (3) were provided for each of the two feed-gas streams for close temperature control. A small gas compressor (7), a rotameter (5), and a heater (3) were provided for the gas recycle stream. The outlet gas was cooled and passed through the condenser (8). The condensate was separated and collected in a receiver (9) and then measured (10). Samples of the outlet gas were collected for analysis (12) and the outlet gas volume was measured with a wet test meter (13).

Chromel-Alumel thermocouples (4) were used to measure the catalyst bed temperatures. Skin thermocouples (thermocouples welded to the outside of the tube) were used to measure the intermediate bed temperatures. Inlet, outlet, and two midpoint bed temperatures were sensed by thermocouples immersed in the gas stream. The temperatures were measured and recorded by a 24-point strip chart recorder.

Sample connections were provided at the 1/3 and 2/3 intermediate points in the catalyst bed. These connections consist of 1/4-in. stainless steel tubes welded to the chamber wall.

## 2. Fabrication of the Reactor for the Reduction of Carbon Monoxide with Hydrogen

The catalyst tube (bed) was fabricated from a 4-ft piece of 5/8-in. OD, 0.049-in. wall, 316 stainless steel tube. Three 1-ft sections of stainless steel (serrated, 1-1/4 in. OD, 4 fins/ft) fins were attached to the outside of the tube. Figure 2 is a photograph of the reaction unit under construction. In the photograph, the lower heating unit is being installed at the bottom of the tube. The lower air inlet connection was installed as shown. It is partly covered by insulation. The cooling air enters at the bottom, flows up around the stainless steel fins, and leaves at the top of each heating unit.

The carbon monoxide, hydrogen, and recycle gas preheaters can be seen at the top of the photograph. Electric heaters similar to the bed heaters were later installed on the preheaters. The product gas cooler-condenser (lower right of photograph) is constructed of a 3-ft-long coil of 3/8-in. stainless steel tubing in a 4-in. OD stainless steel jacket. The condensate separators are made from standard 125-ml stainless steel sample containers.

Figure 3 is a photograph of the completed reaction unit. The reactor and preheaters have been covered with a 3-in. layer of insulation and a stainless steel jacket. A wet test meter (lower right) was used with rotameters and orifices (not shown) to calibrate the flows of the reactant gases and to measure the product gas. The condensate was collected in a 250 ml flask which was periodically weighed. A panel board (left side of photograph) was installed to mount the major instrumentation, including reactor bed pressure indicator-controller, reactor bed pressure drop recorder, temperature recorder (24-point strip chart), reactor catalyst bed temperature controllers, reactant gas preheater controllers, and pressure gages. Two-stage pressure-reducing regulators were mounted on the gas cylinders (not shown). The two reactant gas rotameters and orifices and manometers are mounted on the bench rack back of the panel board. The three cooling air rotameters and needle valves are also located on the bench rack to the left of the reactor (behind the panel board).

### C. TASK 3, TESTING

#### 1. Equipment Operational Limits

A series of short tests was made on the equipment in order to determine its operating limits and characteristics. Argon was used through both preheaters and through the reactor (no catalyst) to establish that reaction temperatures as high as  $900^{\circ}\text{C}$  can be obtained. The temperature on each of the three catalyst bed sections can easily be controlled independently to within as little as  $\pm 2^{\circ}\text{C}$  or to as much as  $\pm 200^{\circ}\text{C}$  of each other.

The catalyst bed pressure-control system was found to operate satisfactorily at pressures up to about 90 psig. With minor changes the equipment can be made to function from 7 psia up to 265 psia. Reactant flow rates can be accurately measured and controlled at rates as low as 0.5 scfh and as high as 10 scfh.

#### 2. Catalyst Reductions

After the apparatus was tested for gas leaks at 100 psig, the reactor tube was filled with 138.5 cc (ca. 65 g) of catalyst. The bed temperature was slowly raised to  $450^{\circ}\text{C}$  and then maintained between 350 and  $450^{\circ}\text{C}$  with 1.0 atm of hydrogen passing over the catalyst. These conditions were maintained

for periods up to 48 hours. A sample of exit gas was taken periodically for water analysis. The water content of the gas decreased with time; catalyst regeneration was considered complete when the water content of the gas dropped below 0.1 vol%. Hydrogen (60 psig) was maintained in the apparatus when it was not in operation.

### 3. Preliminary Runs with Carbon Monoxide and Hydrogen

Several highly successful preliminary test runs were made using Catalyst C-0765-1005. These data are presented in Tables 1, 2, and 3. These preliminary runs were made with a 4:1 hydrogen/carbon monoxide mole ratio (2 scfh of hydrogen and 0.5 scfh of carbon monoxide) at 1.0 atm. The temperature profiles in the catalyst chamber were irregular but the conversions and yields were good. The overall material balances were excellent (to  $\pm 1\%$ ). The individual component balances, however, were not as good, indicating that the operating and analytical techniques needed to be improved.

The operating data for the three preliminary runs are presented in Table 1; Table 2 presents the product gas analyses (mass spectrometer). The hydrogen concentration in the product gas varied from about 63 to 70% and the methane concentration from about 25 to 33%. Ideally, with a 4:1 hydrogen/carbon monoxide mole ratio, the composition should be 50% methane and 50% hydrogen. The carbon monoxide concentration varied from about 0.5 to 0.2%, corresponding to carbon monoxide conversion of 98.6 to 99.4%. The carbon dioxide concentration varied from about 5 to 1%. Only inconclusive traces of  $C_2$  or heavier hydrocarbons were rarely found in the product gas. The water which was condensed from the product gas was clear and colorless; vapor-phase gas chromatographic analysis showed that no carbon-containing compounds were present.

Table 3 presents the material balances and conversions for the runs. Carbon monoxide conversions were very good (98.6 to 99.4%). Yields of methane were fairly good (81.7 to 94.1%). Yields of water were good (85.5 to 90.1%) and yields of carbon dioxide were gratifyingly low (3.2 to 10.8%), compared with up to 25 or 30% reported in the literature. Run 5, with low temperatures in the top section and high temperatures in the bottom section of the bed, was found to give better yields of methane and water than Runs 8 and 9, in which the temperatures were all at 300°C or lower.



#### D. TASK 4, DATA ACQUISITION

Three different catalysts were investigated in order to determine the most efficient one available for reducing carbon monoxide into methane and water. The effects of a bare tube on the reaction were explored, and the effects of impurities in the feed upon the catalyst were investigated. These studies will now be discussed in the order in which they were carried out.

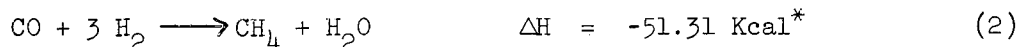
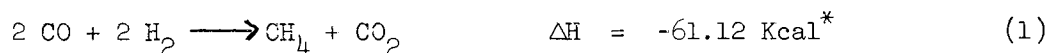
##### 1. Catalyst C-0765-1005

A series of 26 successful data-producing runs was made (Runs 10 to 13, 18 to 33, and 35 to 41) with the C-0765-1005 catalyst (25% Ni on 4 to 8 mesh silica gel). The data for these runs are presented in Tables 4, 5, and 6, and Figures 4 to 9.

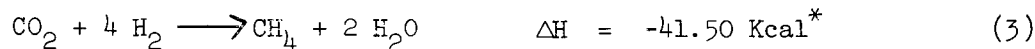
##### a. Temperature

Figure 4 is a plot of the data showing how catalyst temperature affects carbon monoxide conversion and yields at a 4:1 hydrogen/carbon monoxide mole ratio at atmospheric pressure and a  $500 \text{ hr}^{-1}$  space velocity. In this plot the normalized yields were used (see Table 6 and discussion under Material Balances).

There are at least two routes which the reaction of carbon monoxide and hydrogen to yield methane can follow:



Reaction (1) yields carbon dioxide and Reaction (2) yields water as the secondary products. An excess of hydrogen enhances the formation of the products of Reaction (2) by promoting Reaction (3), which consumes the carbon dioxide produced by Reaction (1).



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\* Heat of reaction calculated at  $227^\circ\text{C}$  using JANAF data.

The data in Figure 4 show that as the temperature is increased from 350 to 425°C, the yield of methane and water increased and the carbon dioxide yield decreased. This would occur normally due to an increase in the reaction rate with temperature. However, above 425°C the yield of methane and water decreased and the yield of carbon dioxide increased. This change indicates that either the catalytic activity of the C-0765-1005 catalyst changes in such a manner as to favor carbon dioxide formation above 425°C, or the chemical equilibrium for the overall reaction shifts in favor of carbon dioxide formation at the higher temperatures. The latter seems unlikely as the formation of carbon monoxide, rather than carbon dioxide, is favored by high temperature.

The second charge of catalyst (dotted lines in Figure 4) appeared to be more active than the first charge which was heated to higher temperatures in the preliminary runs. Excellent yields of 98 to 99% water and methane, and less than 1% carbon dioxide, were found to be obtainable with active catalyst.

b. Pressure

Figure 5 shows the effect of catalyst bed pressure on carbon monoxide conversion and yields. A series of runs was made with Catalyst C-0765-1005 with a 4:1 hydrogen/carbon monoxide mole ratio, a 1000 hr<sup>-1</sup> space velocity, and a 450°C bed temperature. Under these conditions, the carbon monoxide conversion was virtually complete at 1 atm; raising the bed pressure to 6 or 7 atm increased the carbon monoxide conversion only slightly. However, increasing the bed pressure had a dramatic effect on product distribution: the water yield increased from 85 to 99+%; the methane yield increased from 93 to 99+%; and the carbon dioxide yield decreased from 7% to less than 0.5%.

In comparing the carbon monoxide conversion in the runs previous to Run 25 with those after Run 25, the data show that the later runs appear to have better carbon monoxide conversions. The actual carbon monoxide conversions in the first 25 runs are believed to be slightly low. The method of analyzing for carbon monoxide in the product gas was changed from mass spectrophotometry to gas chromatography after Run 25. It was found that there was a small amount of nitrogen in the carbon monoxide feed. This nitrogen passed

through the catalyst unchanged and caused the mass spectrometric analysis for carbon monoxide to be 0.2 to 0.3% high. The gas chromatograph separates the carbon monoxide from nitrogen and is sensitive to about 0.01% carbon monoxide. The mass spectrograph cannot perform a similar analysis nearly as easily and was not used for this determination after Run 25.

c. Hydrogen/Carbon Monoxide Mole Ratio

Figure 6 shows the effect of lowering the hydrogen/carbon monoxide mole ratio on carbon monoxide conversion and product yields. Two series of runs were made, one at 1.0 atm pressure and a  $500 \text{ hr}^{-1}$  space velocity, and one at 6.1 atm pressure and at  $1000 \text{ hr}^{-1}$  space velocity. Lowering the hydrogen/carbon monoxide mole ratio from 4:1 to 3.1:1 (at  $500 \text{ hr}^{-1}$  space velocity and 1.0 atm) lowered the water and methane yields severely (95.9% to 78.5%, and 98.1% to 88.4%, respectively) while increasing the carbon dioxide yield 5-fold (2.1 to 10.9%). At the same time the methane concentration of the product gas increased from 48.9 to 56.8% (see Table 5, Runs 20 and 21), a relatively small change.

The series of runs made at  $1000 \text{ hr}^{-1}$  space velocity and at 6.1 atm catalyst bed pressure gave similar results. Increasing the pressure to 6.1 atm more than offset the increase in space velocity from  $500 \text{ hr}^{-1}$  to  $1000 \text{ hr}^{-1}$ , so that the methane and water yields did not drop off quite as fast with decreasing hydrogen/carbon monoxide mole ratio as it did with the 1.0 atm runs. At either pressure, hydrogen/carbon monoxide mole ratios of about 4:1 were required to reduce the carbon dioxide yield to an acceptable level (1 to 2%).

Product gas composition (dry basis) is directly affected by the hydrogen/carbon monoxide mole ratio used. For ideal conversion, a 3:1 feed gas ratio would yield 100% methane and 0% hydrogen, and a 4:1 ratio would yield 50% methane and 50% hydrogen. The actual product gas composition depends upon catalyst activity, space velocity, pressure, temperature, etc. Figure 7 shows how the actual product gas composition varied vs hydrogen/carbon monoxide mole ratio for Catalyst C-0765-1005 at  $450^{\circ}\text{C}$ , 6.1 atm, and 750 to  $1000 \text{ hr}^{-1}$  space velocity. At a 4:1 ratio the product gas (46%  $\text{CH}_4$ , 54%  $\text{H}_2$ ) approached theoretical, but as the hydrogen/carbon monoxide mole ratio was lowered the

product gas composition moved farther and farther from the theoretical. At a 3.05:1 ratio the product gas composition was only 69% methane and 25% hydrogen (theoretical composition, 98.4%  $\text{CH}_4$  and 1.6%  $\text{H}_2$ ). Both carbon monoxide and carbon dioxide in the product gas increased rapidly as the hydrogen/carbon monoxide mole ratio was decreased.

d. Space Velocity

Space velocity, as used in this report, is defined as the reactant flow rate (scfh) divided by the tube volume containing the catalyst (cu ft). Increasing the space velocity from 500 to 1000  $\text{hr}^{-1}$  (at 1.0 atm, 4:1 ratio, and  $450^\circ\text{C}$ ) was found (see Figure 8) to decrease water and methane yield appreciably (95.9 to 89.4%, and 98.1 to 90.3%, respectively) while drastically increasing the carbon dioxide yield (2.1 to 9.2%). The methane content of the product gas also fell (from 48.9 to 33.7%). At catalyst bed pressure of 6.1 atm (at 4:1 ratio and  $450^\circ\text{C}$ ), it was found possible to obtain low carbon dioxide yields at three times the space velocities (see Figure 9) used at 1.0 atm. Figure 8 shows how increasing space velocity affects carbon dioxide yields with several low hydrogen/carbon monoxide mole ratios.

e. Material Balance

The overall material balances (see Table 6) varied from 94 to 103%. In the majority of cases the low material balances are due to water absorbed or condensed out on the catalyst. There are usually at least one or two stations on the catalyst bed which are below the water dew point. The low temperatures are caused by the cooling air which is required to keep the reacting zones at the desired temperature. The section of catalyst below the reacting zone is then cooled below the desired temperature. In future plant designs this problem will be eliminated by providing more cooling fluid inlets so that only the desired sections will be cooled.

Although rather good material balances were obtained ( $\pm 5\%$ ), the rather small changes in water and methane yields vs an independent variable were sometimes partly obscured by the difference in material balance.

Because the material balances vary somewhat above and below 100% and because the yields are directly affected by material balance, it is believed that it is proper to normalize the yields to 100% elemental balance.

Three different methods may be used to calculate product yields. The per pass yield in the case of methane is (moles of  $\text{CH}_4$ /moles of  $\text{CO}$ ) (100); the actual or ultimate yield in this case is (moles of  $\text{CH}_4$ /moles of  $\text{CO}$  - moles of  $\text{CO}$  unconverted) (100). Due to the inherent errors in operating the apparatus with continuously metered inputs and outputs, and with only intermittent sampling of gases for analysis, it is possible that a yield calculated by the above two methods may exceed 100%. Because all of the product appeared either in the gaseous phase or as condensed water, as indicated by the analysis of the catalyst bed after operation, the valid assumption was made that calculated material balances for the elements were in error by the amount they deviated from 100%. Consequently, the actual yield of any product was converted to a more significant yield by making use of this assumption.

An example of this conversion will now be given for Run 13 (Table 6). The actual yield of methane was calculated to be 98.0%. However, the material balance for carbon was calculated to be 104% because the total carbon in the products was found to be 7.469 g per hour whereas the input rate was only 7.17 g of carbon per hour. The methane carbon amounted to 6.954 g of the 7.469 g of total carbon. The amount of carbon in each of the products must be divided by 1.04 to bring the total carbon in the product down to equal 7.17 g. Consequently, the methane actual yield must also be reduced by this factor. The normalized yield is thus calculated as (actual yield/% material balance of major element) (100).

The oxygen balance was used to normalize the water yield because most of the oxygen in the reaction products was contained in the water; the carbon balance was used to normalize the methane yield because nearly all of the carbon in the reaction products was contained in the methane. Although the differences between the actual yields and normalized yields were small, the normalized yields gave a smoother plot of the data than did the actual yields.

Also, the normalized yields approximated more closely the methane and water relationship which is expected when only methane, water, and carbon dioxide are formed.

The material balances were not corrected for the very small amount of carbon that was deposited on the catalyst. Analysis of the catalyst after the completion of Run 13 showed that an insignificant amount of carbon (0.1%) was deposited on the top third of the bed.

f. Heat Balance

The equipment used in these studies was not designed to give accurate heat balances. Accurate heat balances are extremely difficult to obtain in small pilot and bench-scale experiments. However, the overall heat of reaction of the process can be easily calculated from well-known reactions such as those exemplified by Equations (1), (2), and (3). In the apparatus used in this study almost all of the heat of reaction was given off in the top third of the catalyst bed. This was best shown by the amount of cooling air required in the three sections. In none of the runs was any cooling air required in the lower or middle third of the reactor beds, while the top third required up to 40 scfh of 25°C air to control the catalyst bed at the desired temperature (250 to 500°C).

g. Pressure Drop

The pressure drop across the catalyst bed was quite low in all runs when the catalyst was fairly new (see Table 7, Runs 8, 22, 24, 26, and 35). However, after the catalyst had operated for appreciable lengths of time at high temperatures and at low hydrogen/carbon monoxide mole ratios, the carbon deposition on the catalyst greatly increased the pressure drop (see Table 7, Runs 13, 33, and 42). The pressure drop measurement was the best indication of carbon buildup on the catalyst.

h. Catalyst Life

The useful life of Catalyst C-0765-1005 was not accurately determined in these tests. However, judging by the rate of pressure drop

increase across the catalyst bed during the various runs, its useful life would be somewhat limited at the low hydrogen/carbon monoxide mole ratios (less than 3.75:1) and high space velocities (over 1000 hr<sup>-1</sup>). It is believed that the increase in pressure drop was caused by carbon deposition on the catalyst. For example, in Run 41, with a 3.69:1 ratio and a 1480 hr<sup>-1</sup> space velocity, the pressure drop increased from 7.0 to 9.5 in. of water in 4 hours, a rate of about 8% per hour. At a 4:1 ratio and a 500 hr<sup>-1</sup> space velocity, however, no measurable pressure drop was noted in several days of operation. Carefully controlled tests of long duration will be required to determine useful catalyst life.

#### i. Catalyst Bed Depth

These runs were made with a relatively deep catalyst bed (38.5 in.) as compared to 4 to 12 in. for most of the investigations found in the literature. This may, in part, be the reason why such high conversions to desired products were obtained in the work reported herein. Of particular note is the reconversion of carbon dioxide into methane and water.

Table 8 presents representative gas analyses of samples taken from the intermediate catalyst bed sample points. These data indicate that although virtually all of the carbon monoxide was converted in the top section of the bed, the lower 2 ft of the bed were required to convert the carbon dioxide formed in the top 1 ft of the bed into methane and water. This ability to convert carbon dioxide to required product is most important. Every effort was made to eliminate this undesired by-product from the product gas.

#### 2. Catalyst C-0765-1001

A series of 12 data-producing runs was made (Runs 45 to 49, and 51 to 57) with a second kind of catalyst, C-0765-1001 (50% Ni on kieselguhr, 1/8 in. pellets). The data for these runs are presented in Tables 9, 10, and 11, and Figures 10 to 13. This catalyst was so superior to the first catalyst (C-0765-1005) tested that nearly a month was spent evaluating it rather than investigating several other catalysts, as originally planned.

a. Temperature

Time did not permit a thorough study of the effect of catalyst bed temperature with Catalyst C-0765-1001. Some catalyst activity was noted as low as 200°C and the catalyst was found to be very active at 250°C so that very excellent conversions were obtained. Therefore, all of the runs were made at a nominal catalyst bed temperature of 250°C, except Run 57 which was made at 350°C. An attempt was made during Run 57 to increase the conversion by increasing the temperature at a 3:1 hydrogen/carbon monoxide mole ratio and a 1500 hr<sup>-1</sup> space velocity; contrary to expectations, the conversion of carbon dioxide to methane and water decreased as the temperature was increased.

b. Pressure

The first nine runs were made at atmospheric pressure. The conversions were nearly complete at a 4:1 ratio even with space velocities of 2000 hr<sup>-1</sup>. It was only at lower hydrogen/carbon monoxide mole ratios that the conversions decreased sufficiently to require raising the catalyst bed pressure. The last three runs were made at 6.1 atm to approach complete conversion at a 3:1 ratio. In comparing Runs 54 and 55 (see Table 10) it can be seen that increasing the pressure from 1 to 6 atm decreased the carbon dioxide yield from 0.8 to 0.4% and correspondingly increased the yields of water and methane.

c. Hydrogen/Carbon Monoxide Mole Ratio

The effect of hydrogen/carbon monoxide mole ratio on conversion and yields can be seen in Figure 10. At a space velocity of 1000 hr<sup>-1</sup>, at 250°C, and 1.0 atm, the C-0765-1001 catalyst gave complete conversion of carbon monoxide and carbon dioxide until the hydrogen/carbon monoxide mole ratio was decreased to less than 3.5:1. The carbon monoxide conversion remained complete but the carbon dioxide yield increased; at a 3:1 ratio the carbon dioxide yield was approximately 2%.

A reaction, performed under similar conditions using a 1:1 ratio, initially yielded a 1:1 mole ratio mixture of methane and carbon dioxide. The reaction gradually went out of control due to excessive heat release and carbon deposition on the catalyst.



The effect of hydrogen/carbon monoxide mole ratio on the product gas composition can be seen from Figure 11. No carbon monoxide could be detected in the outlet gas for any of these runs. Within this range, the carbon dioxide content of the gas increased logarithmically as the hydrogen/carbon monoxide mole ratio was decreased below 3.5:1 (to ca. 1.5% at 3:1). The theoretical product yield at a 3:1 ratio is 100% methane, 0% hydrogen. The C-0765-1001 catalyst gave 86% methane, 13% hydrogen at the 3:1 ratio. This was much better than the 68% methane, 28% hydrogen obtained using the C-0765-1005 catalyst at the same mole ratio and space velocity, and at higher temperature and pressure.

#### d. Space Velocity

Figure 12 shows how the space velocity affects the yield of carbon dioxide under various conditions with the C-0765-1001 catalyst. At a 4:1 ratio, no carbon dioxide was formed at space velocities up to 2000  $\text{hr}^{-1}$ . At a 3:1 ratio, the carbon dioxide yield increased rapidly as the space velocity was increased above 1000  $\text{hr}^{-1}$ .

#### e. Material Balance

With the exception of two runs, all overall material balances for the runs with the C-0765-1001 catalyst (see Table 11) were under 100%. Most of the low material balances can be attributed to low water recoveries. Because the catalyst is known to be a good adsorbant for water, it has been hypothesized that some of the water is slowly adsorbed on the catalyst. In order to prove that this was the case, a long duration run (Run 49) was made (see Figure 13). The water production, which fluctuated about  $\pm 0.5$  g/hour, gradually increased throughout the run (dotted line). After 30 hours the liquid water production rate was 19.2 g/hour (ca. 96% of theoretical). At the rate of increase of water production (0.01 g/hour), it would have taken about 100 hours before the actual water production rate equalled the theoretical production rate. For long runs, the water balance should be no problem and it is hypothesized that the small amount of water adsorbed on the catalyst may help to prevent carbon formation.

f. Heat Balance

In all runs the majority of the heat was released in the top third of the bed; however, in several runs at high space velocity (1500 or 200  $\text{hr}^{-1}$ ) and/or low hydrogen/carbon monoxide mole ratios (3:1), enough heat release took place in the second third of the catalyst bed to require some cooling. At the highest space velocities (1500 and 1000  $\text{hr}^{-1}$ ), temperature control was very difficult, due to the large amount of cooling air required (up to 100 scfh) to maintain the nominal catalyst bed temperature. In future designs this problem will be solved either by providing multiple carbon monoxide entry points or by providing multiple cooling fluid entrances.

g. Pressure Drop

The pressure drop across the catalyst bed with the pelletized C-0765-1001 catalyst was much lower ( $1/2$  to  $1/4$  as much at the same space velocity and pressure) than it had been with the 4 to 8 mesh C-0765-1005 catalyst (see Table 12).

The pressure drop did not go up with time even at hydrogen/carbon monoxide mole ratios as low as 3:1. Run No. 49 was continued for 31 hours without shutdown; the pressure drop did not increase a measurable amount during this prolonged period. The absence of a pressure buildup indicated no carbon deposition and a long, useful catalyst life.

h. Catalyst Life

Catalyst C-0765-1001-1 was still active when it was removed after 14 runs (110 hours). As can be seen from the tabulation below, analyses on the catalyst before and after use showed no carbon deposition.

Time (hr)	Carbon Content of
	Catalyst C-0765-1001-1 (wt%)
0	5.08
110, Top $1/3$	5.02
110, Mid $1/3$	5.11

As stated previously, there was no pressure buildup during the run so this would not be a limiting factor on the life of the catalyst. However, impurities in the feed (discussed later) may prove to be the limiting factor in the life of this catalyst. Temperature control is also very vital because carbon is definitely deposited on the catalyst at higher ( $400^{\circ}\text{C}$  and up) temperatures. Catalyst life would probably be extended if the catalyst bed operating temperatures were started low when the catalyst is new and active and then gradually raised as the catalyst activity declines.

#### i. Catalyst Bed Depth

At low space velocities only the top inch or two of the catalyst bed was involved in the major portion of the reaction. As the space velocity was increased more and more of the bed was involved until, at very high space velocities and low hydrogen/carbon monoxide mole ratios (Runs 55 and 57), the full length of the catalyst bed was not able to achieve complete conversion of carbon dioxide into methane and water. This is best shown by carbon dioxide gradients in the reactor taken for the various runs as reported in Table 13.

Two additional advantages of a deep catalyst bed are:

(1) it allows for a margin of safety as the catalyst ages and becomes less active; and (2) it allows the top of the bed to act as a guard chamber to remove various catalyst poisons.

#### 3. Catalyst C-0765-1003

A third and final catalyst, C-0765-1003 (15% nickel deposited on kieselguhr, 5/32 in. extruded pellets) was evaluated. The data are presented in Tables 14, 15 and 16 (Runs 60 and 61 only).

##### a. Temperature

The first run was made at  $250^{\circ}\text{C}$  and almost no conversion was obtained. At  $350^{\circ}\text{C}$  (Run 60) excellent conversions were obtained at a 4:1 hydrogen/carbon monoxide mole ratio at 6.1 atm and a  $1000\text{ hr}^{-1}$  space velocity. During Run 61 the temperature was raised to nearly  $400^{\circ}\text{C}$  in an effort to get good conversions at a 3:1 ratio. Only fair conversions were obtained (90%  $\text{H}_2\text{O}$  yield, 95%  $\text{CH}_4$  yield).

b. Pressure

The runs were made at 6.1 atm in an attempt to get maximum conversions.

c. Hydrogen/Carbon Monoxide Mole Ratio

Good conversions were achieved at a 4:1 ratio, but only fair conversions were obtained at a 3:1 ratio.

d. Space Velocity

Only a medium space velocity ( $1000 \text{ hr}^{-1}$ ) was tried. Catalyst C-0765-1003 was less active than Catalyst C-0765-1001; no other space velocities were evaluated.

e. Material Balance

The material balances were excellent for the runs with Catalyst C-0765-1003. Water was not held up on the catalyst to nearly as great an extent as it was on Catalyst C-0765-1001. This resulted in better material balances.

f. Heat Balance

Most of the heat was released in the top third of the catalyst bed; however, an appreciable amount of heat was also released in the middle third of the catalyst bed during Run 61 carried out with a 3:1 ratio.

g. Catalyst Life

The runs were too short to determine catalyst life. However, temperature changes during the runs did indicate that the top third of the bed had started to lose some activity.

h. Catalyst Bed Depth

This catalyst was less active than Catalyst C-0765-1001 so that more of the bed depth was used for conversion at comparable space velocities and hydrogen/carbon monoxide mole ratios.

#### 4. Impurities in the Feed Gas

Most catalysts are known to be subject to poisoning by various impurities. Nickel is known to be poisoned by sulfur and phosphorus. Therefore, it was necessary to determine the extent that these and other poisons can be tolerated in the reactant gases.

##### a. Sulfur

Almost any form of sulfur in the reactant gases will be converted to nickel sulfides and thereby poison the catalyst and reduce its activity. Carbonyl sulfide (COS) was selected for evaluation for convenience and its stability in steel gas cylinders. A high concentration of sulfur in the hydrogen reactant gas (0.1 vol% COS or 59 grains of sulfur per 100 scf) was used in these tests. This concentration is approximately 1000 times the normal allowable limit of sulfur in the feed gas to Fischer-Tropsch units and permitted the extent of sulfur poisoning of the catalyst to be determined in a relatively short time (22 hours).

Run 63b (see Tables 14, 15, and 16) was made with freshly reduced C-0765-1001 catalyst to provide a basis for comparison at a fairly high space velocity and a low hydrogen/carbon monoxide mole ratio. Run 64 was made with 0.1 vol% COS in the hydrogen stream. The data for Run 64c (see Table 16) were taken after 22 hours of operation with 0.1 vol% carbonyl sulfide in the hydrogen stream. In this length of time, 3.08 g of sulfur - equivalent to 3.9 wt% of the nickel in the catalyst - was charged to the catalyst bed, and the product gas composition had changed only slightly ( $\text{CH}_4$  yield dropped from 98.9 to 98.2%,  $\text{H}_2\text{O}$  yield dropped from 97.5 to 96.4%, and  $\text{CO}_2$  yield increased from 0.95 to 1.95%). During the progress of the run, the activity in the top 6 in. of the catalyst bed was observed to gradually decrease. This was evident by the downward movement on the catalyst column of the major temperature peak. Analysis of the catalyst after the run showed that almost all of the sulfur was removed in the first 6 in. of the bed, leaving the balance of the 32 in. for near-normal conversion.

<u>Column Section</u>	<u>Analysis</u>
0 to 3 in. of catalyst	13.4 wt% sulfur
3 to 6 in. of catalyst	10.0 wt% sulfur
6 to 9 in. of catalyst	1.0 wt% sulfur

There was about 50% nickel in the catalyst at the beginning of the evaluation. Hence, the composition in the first 3 in. of the bed approaches  $\text{Ni}_3\text{S}_2$ , which contains 26.6% sulfur.

b. Oxides of Nitrogen

A newly reduced batch of catalyst was used for Run 66 (see Tables 14, 15, and 16) in which 1 vol% nitrogen oxide (NO) was added to the hydrogen stream. The data for Run 66b were taken after approximately 7 hours of operation; at a 2.98:1 hydrogen/carbon monoxide mole ratio, good conversion was obtained (for this low ratio). The data for Run 66c were taken after about 10 hours of operation; at a 3.44:1 ratio, conversions were 100% to methane and water, showing that the catalyst was not damaged. The temperature peak did not progress down the column during the run. It was, therefore, concluded that this nitrogen oxide would not injure the catalyst.

The nitrogen oxide was reduced under the conditions of the reaction. About 2 wt% ammonia was found in the water condensed out from these runs. Additional nitrogen and ammonia were also found in the vapor phase. The nitrogen material balances showed that about 75 wt% of the nitrogen oxide was converted to ammonia, the balance being converted to nitrogen.

c. Phosphorus

In Run 67 (see Tables 14, 15, and 16), 0.5 vol% phosphine ( $\text{PH}_3$ ) was added to the hydrogen stream. This run was stopped after less than 3 hours of operation, at which time the catalyst activity was falling and the pressure drop across the reactor was increasing rapidly (0 to 30 in.  $\Delta P$  in 30 min). In Run 67b, in which the data were taken after about 2 hours of operation, the conversion was still good but it was starting to drop off rapidly. Inspection of the catalyst from the run showed that the majority of the phosphorus

was deposited on the first third of the bed; the second third of the bed contained some phosphorus, and the bottom almost none. The data show that phosphorus is a most active catalyst poison and it will have to be removed from the reactants prior to contact with the nickel catalyst.

d. Other Impurities

Time did not permit the study of other possible poisons. High concentrations of water in the reactants are known to adversely affect column equilibrium if not to actually poison the catalyst. Carbon dioxide is not a poison; it is normally present to some extent in the product gases. Nitrogen gas and ammonia have also been present in low concentrations without damage to the catalyst.

5. Bare Tube Runs (No Catalyst)

A series of runs was made without any catalyst in the reactor to determine whether thermal conversion is practical. The runs (68a, b, c and d, see Tables 14, 15, and 16, and Figure 14) were made with a low space velocity ( $550 \text{ hr}^{-1}$ ), high pressure (6.1 atm) and high hydrogen/carbon monoxide mole ratio (3.7:1) to obtain the highest possible yields. The data show (see Figure 14) that almost no conversion was obtained at  $500^{\circ}\text{C}$ . They show also that the maximum carbon monoxide conversion (about 44%) was achieved at about  $700^{\circ}\text{C}$ , and that at temperatures above  $800^{\circ}\text{C}$  the conversion drops off rapidly. The yield (ultimate) of carbon dioxide is very high (15 to 25%), so that the yields of methane and water are correspondingly low. Appreciable quantities of carbon (1 to 2 g) were found in the tube after the runs so that some cracking of the carbon oxides and/or methane occurs at temperatures of 800 to  $900^{\circ}\text{C}$ . This method of reduction does not offer a solution to the problem at hand (i.e., the quantitative reduction of carbon monoxide with hydrogen to methane and water).

6. Discussion of Results

All three catalysts studied were found to catalyze the reduction of carbon monoxide with hydrogen to form methane and water sufficiently well to be useful in the second step of the carbothermal process. The bare tube results indicated that thermal reduction of carbon monoxide to methane and water is impractical for this process.

Of the three catalysts studied, Catalyst C-0765-1001 was by far the best one for use in the carbothermal process. It can operate successfully at the stoichiometric hydrogen/carbon monoxide mole ratio, thereby using the least amount of hydrogen and producing a product gas highest in methane. It is also capable of yielding a product gas containing no carbon monoxide and little or no carbon dioxide. These carbon oxides would act as diluents in the recycle stream. Finally, Catalyst C-0765-1001 operates at an unusually low temperature which minimizes carbon formation, prolongs catalyst life, and produces no higher molecular weight hydrocarbons or other impurities in either the gas or liquid phase.

Catalyst C-0765-1001 contains a maximum quantity of active nickel (50% by weight) so that a given catalyst bed can tolerate a maximum amount of impurity such as sulfur before it is rendered inactive. Although sulfur will have to be removed from the reactant gases, the tolerable level of sulfur may be higher than once supposed. Phosphorus quickly poisons and degrades the catalyst so that it should be completely scrubbed from the reactant gases. Oxides of nitrogen, if present in the reactant gases, would be reduced.

The equipment which was designed and built for this program has proved to be very effective and flexible for the reduction of carbon monoxide and hydrogen. The equipment will have to be modified for long-term tests and is not suitable for lunar operation without major modifications.

#### E. TASK 5, PROCESS INTEGRATION

##### 1. The Aerojet Carbothermal Process for the Manufacture of Oxygen from Lunar Minerals

The Aerojet carbothermal process for the manufacture of oxygen from lunar minerals (see Figure 15) is a three-step process in which hydrogen and methane (or carbon) are continuously recycled. Lunar rock would be charged continuously and oxygen and slag would be the two major products. Any water present in the rock would be recovered. The energy source would be either solar or nuclear-electric. Waste energy would be radiated into space.



The first step in the carbothermal process is the reduction of the silicate material (believed to be a major portion of the lunar minerals) with methane. Demonstration of the feasibility of this step will be undertaken on an extension of Contract NAS 7-225. A brief description of the process and the equipment designed for this study is presented in this section.

The second step in the carbothermal process is the reduction of the carbon monoxide with hydrogen to form methane (recycle) and water. The feasibility of this step has been demonstrated unequivocally on the present program. The equipment used is shown in Figures 1, 2, and 3. A continuing program is required to determine the operating characteristics of the hardware and the catalyst over prolonged time periods (i.e., 60 to 90 days of continuous operation).

The third step in the carbothermal process is the electrolytic reduction of the water to hydrogen (recycle) and oxygen (product). Some of the major problems in this step are (a) reduction in cell weight, (b) increasing the cell efficiency (lower over-voltage), and (c) lower losses of electrolyte and/or electrode. Research and development on this step in the process should be initiated promptly.

## 2. Integration of Steps 1 and 2

After Steps 1 and 2 have been demonstrated separately, the next step will be the development of an integrated system. It will not be necessary to include Step 3 in the integrated plant at this time as the third step can be depended upon to produce 99.9% pure hydrogen which is not measurably different from commercially available hydrogen.

Figure 16 shows a flow diagram for the integration of Steps 1 and 2. Hydrogen, carbon monoxide, and methane would be used to start up Steps 1 and 2 independently. Then the methane and carbon monoxide would be shut off and the gases from Step 1 would be fed directly to Step 2 along with enough hydrogen to make up for the hydrogen that is lost in the production of water. Small amounts of either methane or carbon monoxide would be added to make up for any loss of carbon. The crushed rock (simulating lunar minerals) will be added continuously by means of a variable-speed solids feeder. The slag will be removed intermittently utilizing a heated valve or by continuous removal facilities.

### 3. Design of the Reactor for the Reduction of Silicate Minerals with Methane

The silicate rock reduction furnace shown in Figure 17 was designed for the study of basic engineering considerations. Tubes (1)\* carrying the methane and/or hydrogen into the melt have been carefully sized for velocities and rates of gas feed as related to equipment capacity and reaction period. Methane must be released from the feed tube at a temperature below its cracking temperature, approximately 1000°C.

Heat is supplied by means of induction electrical current, 450 kc frequency (2). The reactor materials accordingly have been selected to have minimum effect on the electrical field. A radiometer head (3) controls the temperature of the tungsten crucible (4) which will contain the rock melt.

Facilities are provided for evacuating the reactor and purging with argon before feeding in the normal methane/hydrogen atmosphere. Evacuation and argon purge will precede shutdown also. The vacuum pump (5) will normally be idle and valve (6) closed to the system.

Fine regulation of gas flow has been provided by manometers, pressure gages and orifice plates for methane (7), and hydrogen (8). A wet test meter (9) provides product gas measurement.

A gas chromatograph (10) monitors the carbon monoxide, hydrogen, and methane content of the exit gas. Water is extracted ahead of the chromatograph by drying tubes (11). As carbon dioxide should only be present, if at all, during initial melting of the rock, an ascarite tube (12) is provided for its quantitative collection. A sample station (13) provides for mass spectrograph, or similar type of analysis, to be made at a different location.

The rock reactor is provided with temperature control (14) at its midpoint. An optical pyrometer (15) provides temperature indication for the rock melt. A thermocouple (15) provides temperature of gas inlet to rock melt.

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\* Numbers refer to coding system used in Figure 17 to label reactor components.

The rock reductions will initially be studied by melting in aluminum oxide (99.5%  $\text{Al}_2\text{O}_3$ , working temperature  $1950^\circ\text{C}$ ) or zirconium oxide crucibles. These crucibles (not shown) sit inside the tungsten crucible (4), acting as the furnace liner. Zirconia (16) insulation is provided between the tungsten crucible and quartz retaining cylinder (17). The melt is viewed by remote lens and mirror (18). The rock reactor is enclosed by a Pyrex bell jar. Cooling is provided by air streams plus the water-cooled induction coil (19) and water condenser (20). The reactor is enclosed in a safety shield. Additional safety has been provided by using metallic piping and valves as much as possible. A system pressure relief is provided (21). A flame arrester (22) is placed on the outlet gas line to protect the system.

#### IV. PERSONNEL

The senior staff primarily assigned to this program was comprised of S. D. Rosenberg (Project Manager), G. A. Guter, F. E. Miller, M. Rothenberg, and G. R. Jameson.

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**TABLE 1**  
**REDUCTION OF CARBON MONOXIDE WITH HYDROGEN,**  
**PRELIMINARY RUNS**  
**(OPERATING DATA)<sup>a</sup>**

Run No.	Reactant Flow Rate		Product Flow Rate		Inlet Gas Temp (°C)	Catalyst Bed Temperature			Outlet Gas Temp (°C)
	H <sub>2</sub> (scfh)	CO (scfh)	Gas (scfh)	H <sub>2</sub> O(l) (g/hr)		Top (°C)	Mid (°C)	Bottom (°C)	
5	2.02	0.48	1.39	9.1	220	178	311	541	228
8	2.00	0.50	1.57	8.8	281	280	275	278	170
9	2.00	0.50	1.28	8.2	240	259	300	299	169

<sup>a</sup> Catalyst: C-0765-1005; Bed Pressure: 1 atm.

TABLE 2  
REDUCTION OF CARBON MONOXIDE WITH HYDROGEN,  
PRELIMINARY RUNS  
(PRODUCT GAS ANALYSIS)<sup>a</sup>

Run No.	Composition of Product Gas (vol%)				
	H <sub>2</sub>	H <sub>2</sub> O	CO	CH <sub>4</sub>	CO <sub>2</sub>
5	65.4	1.20	0.50	32.0	0.9
8	70.0	1.20	0.30	25.8	2.7
9	63.5	1.20	0.20	30.9	4.2

<sup>a</sup> Three to six gas samples were obtained during the course of each run, at 1- to 2-hour intervals. The average analysis resulting from these samples for each run is reported here. The composition of the gas was determined by mass spectrometric analysis, excepting water vapor. The water vapor concentration was assumed to be fixed by the condenser water temperature (10°C). This assumption was spot-checked periodically by vapor-phase chromatography and was found to be correct. Each gas sample was checked for higher hydrocarbons; none were found. Liquid water samples were spot-checked for carbon-containing compounds; none were found.

TABLE 3

REDUCTION OF CARBON MONOXIDE WITH HYDROGEN,  
PRELIMINARY RUNS  
(CO CONVERSION AND PRODUCT YIELD)

Run No.	H <sub>2</sub> /CO Mole Ratio	Space Velocity <sup>a</sup> (hr <sup>-1</sup> )	Nominal Catalyst Bed <sup>b</sup> Temp (°C)	Overall Material Balance (%)	CO Conversion (mole%)	Actual Product Yield (mole%)		
						H <sub>2</sub> O <sup>c</sup>	CH <sub>4</sub>	CO <sub>2</sub>
5	4.2	503	-	100	98.6	90.1	94.1	3.2
8	4.0	503	278	101	99.4	85.5	81.7	8.5
9	4.0	503	285	101	99.4	88.0	79.4	10.8

<sup>a</sup> Space Velocity =  $\frac{\text{Standard cu ft/hr of reactants}}{\text{cu ft of catalyst}}$

<sup>b</sup> Average of the top, mid, and bottom temperature points of the catalyst bed.

<sup>c</sup> Based on total of liquid and gaseous fractions.

Table 4

TABLE 4  
REDUCTION OF CARBON MONOXIDE WITH HYDROGEN,  
CATALYST C-0765-1005  
(OPERATING DATA)

Run No.	Reactant Flow Rate		Product Flow Rate		Catalyst Bed Pressure (atm)	Inlet Gas Temp (°C)	Catalyst Bed Temperature			Outlet Gas Temp (°C)	Catalyst No.
	H <sub>2</sub> (scfh)	CO (scfh)	Gas (scfh)	H <sub>2</sub> O(l) (g/hr)			Top (°C)	Mid (°C)	Bottom (°C)		
10	2.00	0.50	1.207	8.66	1.0	290	348	350	350	195	C-0765-1005-1
11	2.00	0.50	1.008	9.64	1.0	314	382	399	401	219	
12	2.00	0.50	1.056	9.97	1.0	291	448	451	451	248	
13	2.00	0.50	1.086	9.38	1.0	321	500	500	501	283	C-0765-1005-2
18	2.00	0.50	0.990	10.32	1.0	269	350	351	351	182	
19	2.00	0.50	1.022	10.04	1.0	307	402	403	402	204	
20	2.00	0.50	1.009	10.05	1.0	320	452	451	452	251	
21	2.12	0.69	1.069	11.45	1.0	232	450	451	452	239	
22	2.88	0.88	1.553	13.76	1.0	326	450	453	452	266	
23	2.88	0.88	1.540	13.40	1.0	328	452	453	451	261	
24	3.90	0.96	2.461	14.72	1.0	277	454	452	452	264	C-0765-1005-3
25	3.90	0.96	2.31	16.7	1.0	341	451	451	451	281	
26	3.90	0.96	2.06	19.5	7.1	433	447	452	450	267	
27	3.90	0.96	1.98	19.2	6.1	352	452	452	452	265	
28	3.75	1.23	1.62	21.4	6.1	345	454	452	455	269	
29	2.76	0.85	1.18	18.2	6.1	382	453	452	452	255	
30	1.87	0.57	0.82	11.0	6.1	348	452	452	452	244	
31	1.98	0.50	1.12	8.9	1.0	257	454	451	451	254	
32	3.86	0.97	1.98	19.2	6.1	341	452	453	453	267	
33	3.69	1.12	1.72	21.1	6.1	355	451	453	453	266	
35	3.76	0.96	2.02	19.7	6.1	281	344	399	451	269	C-0765-1005-3
36	3.82	0.97	2.00	20.5	6.1	188	424	400	449	276	
38	5.80	1.44	3.08	29.1	6.1	245	425	445	450	301	
39	3.81	1.01	1.92	19.7	6.1	360	449	452	452	263	
40	3.70	0.99	1.87	19.5	6.1	345	451	452	453	265	
41	5.61	1.54	2.88	28.2	6.1	363	449	443	453	289	



TABLE 5  
REDUCTION OF CARBON MONOXIDE WITH HYDROGEN,  
CATALYST C-0765-1005  
(PRODUCT GAS ANALYSIS)<sup>a</sup>

Run No.	Composition of Product Gas (vol%)				
	H <sub>2</sub>	H <sub>2</sub> O	CO	CH <sub>4</sub>	CO <sub>2</sub>
10	58.97	1.21	0.38	35.84	3.59
11	50.47	1.21	0.34	46.86	1.13
12	52.16	1.21	0.39	45.42	0.82
13	50.95	1.21	0.52	44.54	2.78
18	45.80	1.21	0.33	51.67	0.99
19	51.68	1.21	0.24	46.54	0.33
20	48.51	1.21	0.30	48.96	1.02
21	34.55	1.21	0.50	56.82	6.93
22	41.45	1.21	0.52	50.81	6.01
23	43.36	1.21	0.59	48.85	5.99
24	60.91	1.21	0.69	33.70	3.49
25	56.82	1.21	0.02	39.12	2.83
26	54.66	0.17	0.01	45.14	0.02
27	54.65	0.20	0.01	44.95	0.20
28	25.54	0.20	0.12	69.42	4.72
29	31.23	0.20	0.07	66.47	2.03
30	32.97	0.20	0.02	65.89	0.92
31	55.56	1.21	0.08	41.85	1.30
32	50.72	0.20	0.03	48.72	0.33
33	33.75	0.20	0.12	62.78	3.15
35	53.76	0.20	0.01	45.91	0.10
36	53.55	0.20	0.01	46.14	0.10
38	53.73	0.20	0.03	45.67	0.37
39	50.57	0.20	0.03	48.43	0.77
40	52.06	0.20	0.02	47.12	0.60
41	47.89	0.20	0.15	49.76	2.00

<sup>a</sup> Three to six gas samples were obtained during the course of each run, at 1- to 2-hour intervals. The average analysis resulting from these samples for each run is reported here. The composition of the gas was determined by mass spectrometric analysis, excepting water vapor. The water vapor concentration was assumed to be fixed by the condenser water temperature (10°C). This assumption was spot-checked periodically by vapor-phase chromatography and was found to be correct. During the first 24 runs CO determinations were made by mass spectrometric analysis. In subsequent runs CO analyses were made by gas chromatographic methods which were found to be more sensitive to the extremely low concentrations of CO obtained. Gas samples were checked for higher hydrocarbons; none were found. Liquid water samples were checked for carbon-containing compounds; none were found.

Table 6

TABLE 6  
REDUCTION OF CARBON MONOXIDE WITH HYDROGEN,  
CATALYST C-0765-1005  
(CO CONVERSION AND PRODUCT YIELD)

Run No.	H <sub>2</sub> /CO Mole Ratio	Space Velocity <sup>a</sup> (hr <sup>-1</sup> )	Catalyst Bed Pressure (atm)	Nominal Catalyst Bed Temp (°C)	Overall Material Balance (%)	CO Conversion (mole%)	Actual Product Yield (mole%)			Normalized Product Yield <sup>d</sup> (mole%)	
							H <sub>2</sub> O <sup>c</sup>	CH <sub>4</sub>	CO <sub>2</sub>	H <sub>2</sub> O <sup>c</sup>	CH <sub>4</sub>
10	4.0	503	1.0	350	99.6	99.1	84.2	87.4	8.7	83.1	90.5
11	4.0	503	1.0	394	97.2	99.3	92.6	95.4	2.3	95.2	97.7
12	4.0	503	1.0	450	99.3	99.1	96.1	96.9	1.7	96.6	98.1
13	4.0	503	1.0	500	102.5	89.9	90.8	98.0	6.1	88.3	94.3
18	4.0	516	1.0	351	102.8	99.3	98.9	103.2	2.0	96.2	98.4
19	4.0	516	1.0	402	97.4	99.5	98.0	95.6	0.7	100.1	99.0
20	4.0	516	1.0	452	100.5	99.4	96.5	99.5	2.1	95.9	98.1
21	3.1	580	1.0	451	100.8	99.2	79.8	89.1	10.9	78.5	88.4
22	3.3	778	1.0	452	98.4	99.1	74.8	89.9	10.6	76.9	89.6
23	3.3	778	1.0	452	95.6	99.0	73.1	85.8	10.5	76.5	88.7
24	4.1	1005	1.0	453	96.1	98.2	75.5	89.8	9.1	79.2	90.2
25	4.06	1005	1.0	451	99.3	99.95	83.7	94.2	6.8	85.5	93.3
26	4.06	1005	7.1	450	96.7	99.98	94.7	97.0	0.04	99.8	99.9
27	4.06	1005	6.1	452	94.1	99.98	93.1	92.4	0.4	99.0	99.1
28	3.05	1003	6.1	454	95.6	99.84	80.9	91.4	6.2	85.9	93.3
29	3.25	749	6.1	452	100.9	99.90	99.8	92.2	2.8	94.9	96.9
30	3.32	502	6.1	452	96.4	99.97	90.9	96.7	1.3	96.9	98.6
31	3.96	509	1.0	452	95.7	99.80	85.6	94.8	2.9	92.9	96.9
32	3.99	999	6.1	453	96.8	99.94	92.5	99.9	0.28	99.2	99.7
33	3.03	996	6.1	452	99.6	99.81	87.9	96.8	4.8	89.8	95.3
35	3.94	976	6.1	398	98.1	99.98	96.2	96.9	0.2	99.5	99.8
36	3.95	990	6.1	424	98.7	99.98	98.9	95.6	0.2	99.5	99.8
38	4.03	1499	6.1	440	98.9	99.93	94.3	97.9	0.8	98.2	99.2
39	3.75	998	6.1	451	94.6	99.94	90.9	91.9	1.46	96.6	98.3
40	3.74	970	6.1	452	93.9	99.96	91.9	89.4	1.14	97.4	98.6
41	3.69	1480	6.1	448	96.1	99.72	86.4	94.2	3.78	91.4	96.0

<sup>a</sup> Space Velocity =  $\frac{\text{Standard cu ft/hr of reactants}}{\text{cu ft of catalyst}}$

<sup>b</sup> Average of the top, mid, and bottom temperature points of the catalyst bed.

<sup>c</sup> Based on total of liquid and gaseous fractions.

<sup>d</sup> Based on 100% material balance for oxygen (calculated as water) and for carbon (calculated as methane and carbon dioxide).

**TABLE 7**

**EFFECT OF REACTION TIME ON CATALYST BED PRESSURE DROP,  
CATALYST C-0765-1005**

<b>Run No.</b>	<b>Space Velocity (hr<sup>-1</sup>)</b>	<b>Bed Pressure (atm)</b>	<b>Pressure Drop <math>\Delta P</math> (in. of H<sub>2</sub>O)</b>
8	503	1.0	2.0
22	778	1.0	3.5
24	1000	1.0	8.7
26	1005	7.1	7.0
35	976	6.1	7.5
13	503	1.0	2.8
33	996	6.1	110
42	350	1.0	15.0

TABLE 8

REACTION GAS COMPOSITION<sup>a</sup>,  
CATALYST C-0765-1005

Run No.	Sample Location	Gas Composition (vol%)			
		H <sub>2</sub>	CO	CH <sub>4</sub>	CO <sub>2</sub>
10-4a	Top	70.6	0.4	18.8	4.9
10-4b	Mid	61.1	0.4	34.1	3.9
10-4c	Outlet	58.2	0.3	37.3	3.6
11-6a	Top	-	-	-	6.8
11-6b	Mid	-	-	-	2.4
11-6c	Outlet	54.5	0.3	43.5	1.1
19-3a	Top	-	-	-	6.0
19-3b	Mid	-	-	-	1.3
19-3c	Outlet	54.1	0.1	45.1	0.3
27-a	Top	-	-	-	4.2
27-b	Mid	-	-	-	1.0
27-c	Outlet	54.6	0.01	44.9	0.2
32-a	Top	-	-	-	4.5
32-b	Mid	-	-	-	1.0
32-c	Outlet	50.7	0.03	48.7	0.3
40-a	Top	-	-	-	5.2
40-b	Mid	-	-	-	2.0
40-c	Outlet	52.1	0.02	47.1	0.6

<sup>a</sup> Gas samples were removed from the reactor, 12 and 24 in. from the top of the catalyst bed, respectively, and analyzed. The results are compared with the product gas analysis.

**TABLE 9**  
**REDUCTION OF CARBON MONOXIDE WITH HYDROGEN,**  
**CATALYST C-0765-1001-1**  
**(OPERATING DATA)**

Run No.	Reactant Flow Rate		Product Flow Rate		Catalyst Bed Pressure (atm)	Inlet Gas Temp (°C)	Catalyst Bed Temperature			Outlet Gas Temp (°C)
	H <sub>2</sub> (scfh)	CO (scfh)	Gas (scfh)	H <sub>2</sub> O(l) (g/hr)			Top (°C)	Mid (°C)	Bottom (°C)	
45	1.93	0.482	1.04	9.62	1.0	291	251	249	250	133
46	2.90	0.726	1.47	13.23	1.0	280	248	249	251	140
47	3.89	0.952	2.05	19.24	1.0	289	252	251	253	150
48	5.72	1.443	2.77	28.50	1.0	254	249	254	257	175
49a	3.87	0.955	2.07	19.55	1.0	293	249	249	251	163
51	7.82	1.890	4.12	38.42	1.0	157	305	234	255	202
52b	2.89	1.017	1.08	18.83	1.0	288	246	247	251	147
53	3.77	1.060	1.67	20.88	1.0	270	255	254	254	154
54	3.66	1.164	1.36	23.14	1.0	278	252	256	254	154
55	3.63	1.195	1.27	24.80	6.1	315	257	249	254	162
56	5.42	1.802	1.91	36.58	6.1	255	252	213	256	192
57	5.43	1.796	1.98	36.08	6.1	326	352	354	353	253

TABLE 10

REDUCTION OF CARBON MONOXIDE WITH HYDROGEN,  
CATALYST C-0765-1001  
(PRODUCT GAS ANALYSIS)

Run No.	Composition of Product Gas (vol%)				
	H <sub>2</sub>	H <sub>2</sub> O	CO	CH <sub>4</sub>	CO <sub>2</sub>
45	49.4	1.20	0.0	49.4	0.00
46	49.4	1.15	0.0	49.4	0.00
47	51.5	1.15	0.0	47.3	0.00
48	48.4	1.15	0.0	50.4	0.05
49a	50.8	1.15	0.0	48.1	0.00
51	53.0	1.15	0.0	45.9	0.00
52b	8.9	1.14	0.0	91.5	3.50
53	38.5	1.14	0.0	60.4	0.00
54	17.7	1.14	0.0	80.5	0.65
55	9.3	0.20	0.0	90.2	0.35
56	12.0	0.20	0.0	86.6	1.27
57	18.9	0.20	0.0	78.6	2.25

**TABLE 11**  
**REDUCTION OF CARBON MONOXIDE WITH HYDROGEN,**  
**CATALYST C-0765-1001**  
**(CO CONVERSION AND PRODUCT YIELD)**

Run No.	H <sub>2</sub> /CO Mole Ratio	Space Velocity <sup>a</sup> (hr <sup>-1</sup> )	Catalyst Bed Pressure (atm)	Nominal Catalyst Bed Temp (°C)	Overall Material Balance (%)	CO Conversion (mole%)	Actual Product Yield (mole%)			Normalized Product Yield <sup>d</sup> (mole%)	
							H <sub>2</sub> O <sup>c</sup>	CH <sub>4</sub>	CO <sub>2</sub>	H <sub>2</sub> O <sup>c</sup>	CH <sub>4</sub>
45	4.00	500	1.0	250	101.0	100.0	95.0	106.8	0.0	100.0	100.0
46	4.00	750	1.0	249	93.3	100.0	86.7	99.1	0.0	100.0	100.0
47	4.10	1003	1.0	252	99.0	100.0	96.1	101.7	0.0	100.0	100.0
48	3.96	1481	1.0	253	95.3	100.0	93.8	96.6	0.1	99.8	99.9
49a	4.06	1000	1.0	251	101.0	100.0	97.5	104.0	0.0	100.0	100.0
51	4.15	2010	1.0	265	98.6	100.0	97.0	100.0	0.0	100.0	100.0
52b	2.84	810	1.0	248	98.1	100.0	87.2	97.5	3.7	91.1	96.2
53	3.56	1000	1.0	254	94.5	100.0	93.3	95.3	0.0	100.0	100.0
54	3.14	998	1.0	254	95.0	100.0	93.5	93.8	0.8	98.3	99.1
55	3.03	1000	6.1	253	96.9	100.0	96.3	99.9	0.4	99.2	99.4
56	3.01	1500	6.1	231	95.4	100.0	94.3	91.3	1.3	97.3	98.5
57	3.02	1500	6.1	353	94.8	100.0	93.4	87.0	2.5	94.8	97.1

<sup>a</sup> Space Velocity =  $\frac{\text{Standard cu ft/hr of reactants}}{\text{cu ft of catalyst}}$

<sup>b</sup> Average of the top, mid, and bottom temperature points of the catalyst bed.

<sup>c</sup> Based on total of liquid and gaseous fractions.

<sup>d</sup> Based on 100% material balance for oxygen (calculated as water) and for carbon (calculated as methane and carbon dioxide).

TABLE 12  
 CATALYST BED PRESSURE DROP,  
 CATALYST C-0765-1001

Run No.	Space Velocity (hr <sup>-1</sup> )	Pressure (atm)	Pressure Drop $\Delta P$ (in. of H <sub>2</sub> O)
45	500	1.0	1
46	750	1.0	1
47	1000	1.0	2
48	1480	1.0	3.5
49	1000	1.0	2
51	2000	1.0	6
52	810	1.0	1.5
53	1000	1.0	1.5
55	1000	6.1	> 1
57	1500	6.1	2



TABLE 13

REACTANT GAS CARBON DIOXIDE CONTENT VERSUS CATALYST BED DEPTH,  
CATALYST C-0765-1001

Run No.	Space Velocity (hr <sup>-1</sup> )	H <sub>2</sub> /CO Mole Ratio	CO <sub>2</sub> Analysis (vol %)		
			Top Third	Mid Third	Outlet
45	500	4.0	0.4	0.0	0.00
46	750	4.0	1.6	0.0	0.00
47	1000	4.1	2.7	0.3	0.00
48	1481	4.0	4.6	0.8	0.05
51	2010	4.1	3.8	0.2	0.00
55	1000	3.0	4.9	1.0	0.35
57	1500	3.0	6.1	3.6	2.25

Table 14

TABLE 14  
REDUCTION OF CARBON MONOXIDE WITH HYDROGEN  
(OPERATING DATA)

Reactant Flow Rate				Product Flow Rate				Catalyst Bed Temperature					Catalyst No.	Impurity (Mole% in H <sub>2</sub> Stream)
Run No.	H <sub>2</sub> (scfh)	CO (scfh)	Gas (scfh)	H <sub>2</sub> O(l) (g/hr)	Catalyst Bed Pressure (atm)	Inlet Gas Temp (°C)	Top (°C)	Mid (°C)	Bottom (°C)	Outlet Gas Temp (°C)				
60	3.88	0.962	2.10	21.1	6.1	249	307	387	353	240	C-0765-1003	-		
61	3.62	1.210	1.45	23.6	6.1	262	368	397	398	260	C-0765-1003	-		
63b	3.62	1.210	1.28	25.4	6.1	300	253	254	254	153	C-0765-1001-2	-		
64c	3.62 <sup>a</sup>	1.210	1.25	24.2	6.1	283	256	255	253	228	C-0765-1001-2	0.1 COS		
66b	3.64 <sup>a</sup>	1.210	1.26	25.0	6.1	61	250	260	254	169	C-0765-1001-3	1.0 NO		
66c	4.20 <sup>a</sup>	1.210	1.62	26.6	6.1	60	254	250	251	176	C-0765-1001-3	1.0 NO		
67b	3.74 <sup>a</sup>	1.210	1.32	26.8	6.1	38	267	229	251	189	C-0765-1001-3	0.5 PH <sub>3</sub>		
68a	2.11	0.568	1.98	2.2	6.1	414	604	594	610	338	None	-		
68b	2.11	0.568	1.99	2.8	6.1	442	702	703	700	400	None	-		
68c	2.11	0.568	2.00	3.7	6.1	500	803	806	807	465	None	-		
68d	2.11	0.568	2.30	2.0	6.1	618	903	905	897	474	None	-		

<sup>a</sup> This flow includes the impurity which was added to the hydrogen stream.

**TABLE 15**  
**REDUCTION OF CARBON MONOXIDE WITH HYDROGEN**  
**(PRODUCT GAS ANALYSIS)**

Run No.	Composition of Product Gas (vol%)						
	H <sub>2</sub>	H <sub>2</sub> O	CO	CH <sub>4</sub>	CO <sub>2</sub>	NH <sub>3</sub>	N <sub>2</sub>
60	53.9	0.20	0.0	45.7	0.2	-	-
61	16.4	0.20	0.01	79.2	4.1	-	-
63b	6.0	0.20	0.0	92.9	0.9	-	-
64c	5.0	0.20	0.0	93.2	1.6	-	-
66b	4.0	0.20	0.0	93.3	1.8	0.2	0.5
66c	21.8	0.20	0.0	77.2	0.0	0.3	0.5
67b	10.0	0.20	0.0	88.4	1.4	-	-
68a	71.0	0.20	16.9	8.7	3.2	-	-
68b	70.9	0.20	16.9	9.5	2.6	-	-
68c	71.0	0.20	15.9	10.9	1.9	-	-
68d	75.0	0.20	18.6	5.2	1.0	-	-

Table 16

TABLE 16  
REDUCTION OF CARBON MONOXIDE WITH HYDROGEN  
(CO CONVERSION AND PRODUCT YIELD)

Run No.	H <sub>2</sub> /CO Mole Ratio	Space Velocity <sup>a</sup> (hr <sup>-1</sup> )	Catalyst Bed Pressure (atm)	Nominal Catalyst Bed Temp <sup>b</sup> (°C)	Overall Material Balance (%)	CO Conversion (mole%)	Actual Product Yield (mole%)			Normalized Product Yield <sup>d</sup> (mole%)	
							H <sub>2</sub> O <sup>c</sup>	CH <sub>4</sub>	CO <sub>2</sub>	H <sub>2</sub> O <sup>c</sup>	CH <sub>4</sub>
60	4.02	1000	6.1	349	102.3	100.0	102.1	100.0	0.43	99.2	99.7
61	3.00	1000	6.1	387	100.2	99.9	90.8	94.8	4.90	90.3	95.1
63b	3.00	1000	6.1	254	99.5	100.0	97.5	98.2	0.95	97.6	99.0
64c	3.00	1000	6.1	254	97.1	100.0	92.9	96.5	1.65	96.4	98.2
66b	2.98	1005	6.1	255	98.8	100.0	95.6	96.8	1.87	98.6	97.2
66c	3.44	1120	6.1	252	100.8	100.0	102.2	103.2	0.00	100.0	100.0
67b	3.09	1024	6.1	249	100.6	100.0	103.0	96.2	1.52	97.2	98.2
68a	3.72	553	6.1	603	97.7	40.9	46.0	73.9	27.2	46.0	73.9
68b	3.72	553	6.1	702	99.0	41.0	58.2	82.0	22.2	57.6	81.2
68c	3.72	553	6.1	805	100.0	43.5	71.8	88.3	15.4	71.1	87.4
68d	3.72	553	6.1	902	99.4	24.9	67.6	84.0	16.2	67.6	84.0

<sup>a</sup> Space Velocity =  $\frac{\text{Standard cu ft/hr of reactants}}{\text{cu ft of catalyst}}$

<sup>b</sup> Average of the top, mid, and bottom temperature points of the catalyst bed.

<sup>c</sup> Based on total of liquid and gaseous fractions.

<sup>d</sup> Based on 100% material balance for oxygen (calculated as water) and for carbon (calculated as methane and carbon dioxide).

1 Stainless Steel Fintube, Reaction Chamber

2 Heaters

3 Heaters

4 Thermocouples

5 Flow Indicators

6 Pressure Reducing Regulators

8 Cooler-Condenser

9 Condensate Receiver

10 Graduate Cylinder

11 Back Pressure Regulator

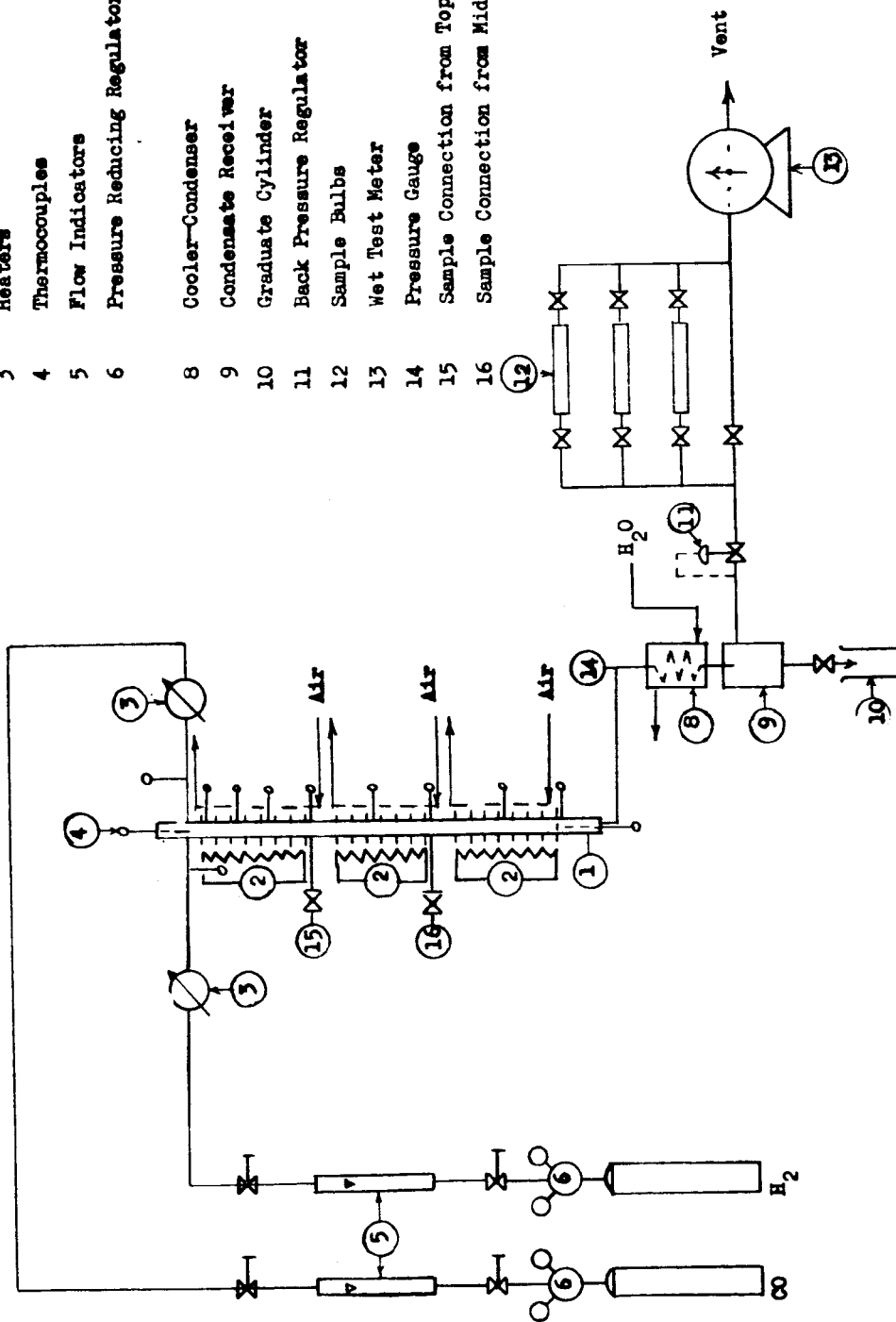
12 Sample Bulbs

13 Wet Test Meter

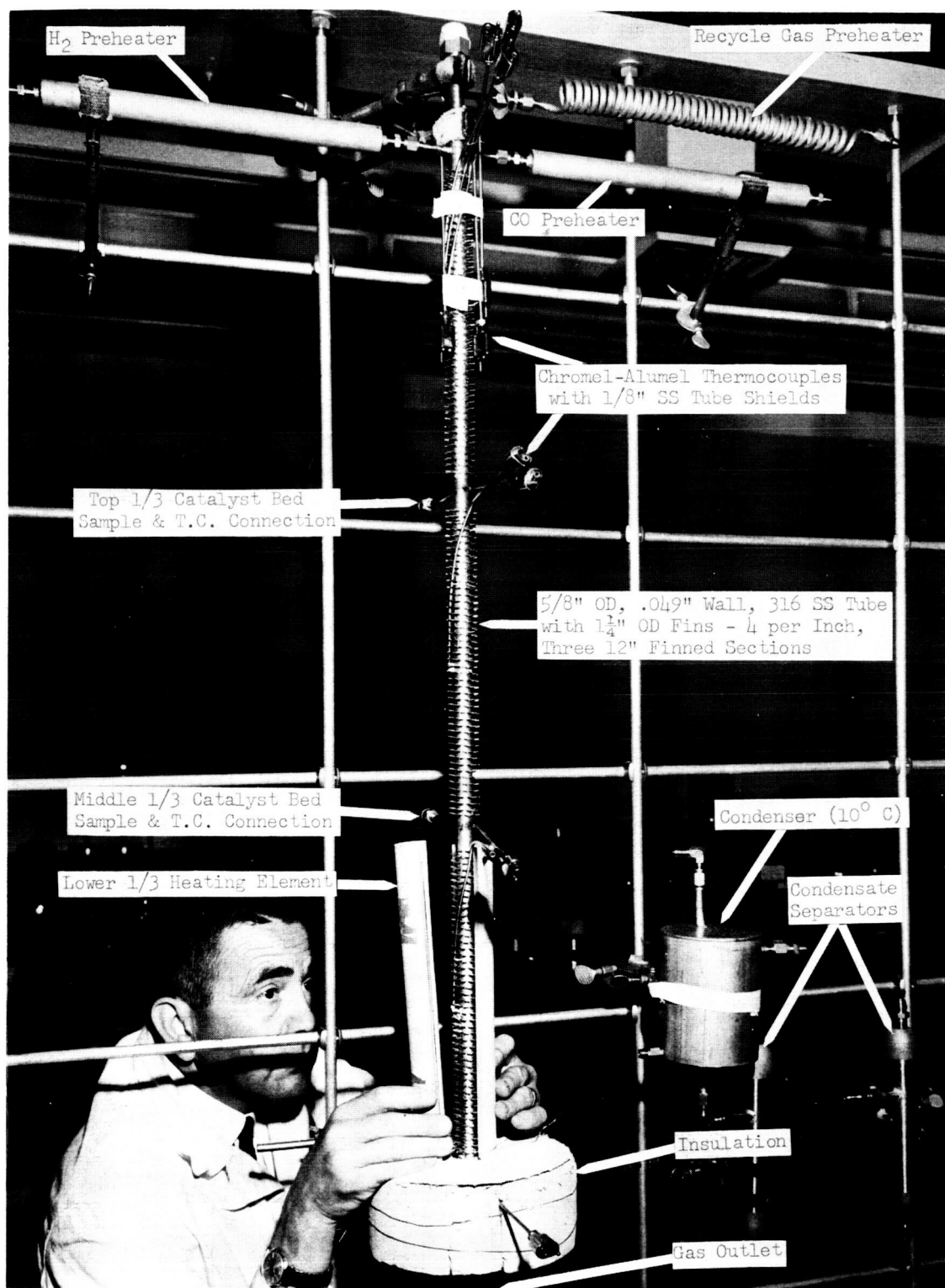
14 Pressure Gauge

15 Sample Connection from Top 1/3 of bed

16 Sample Connection from Middle 1/3 of bed

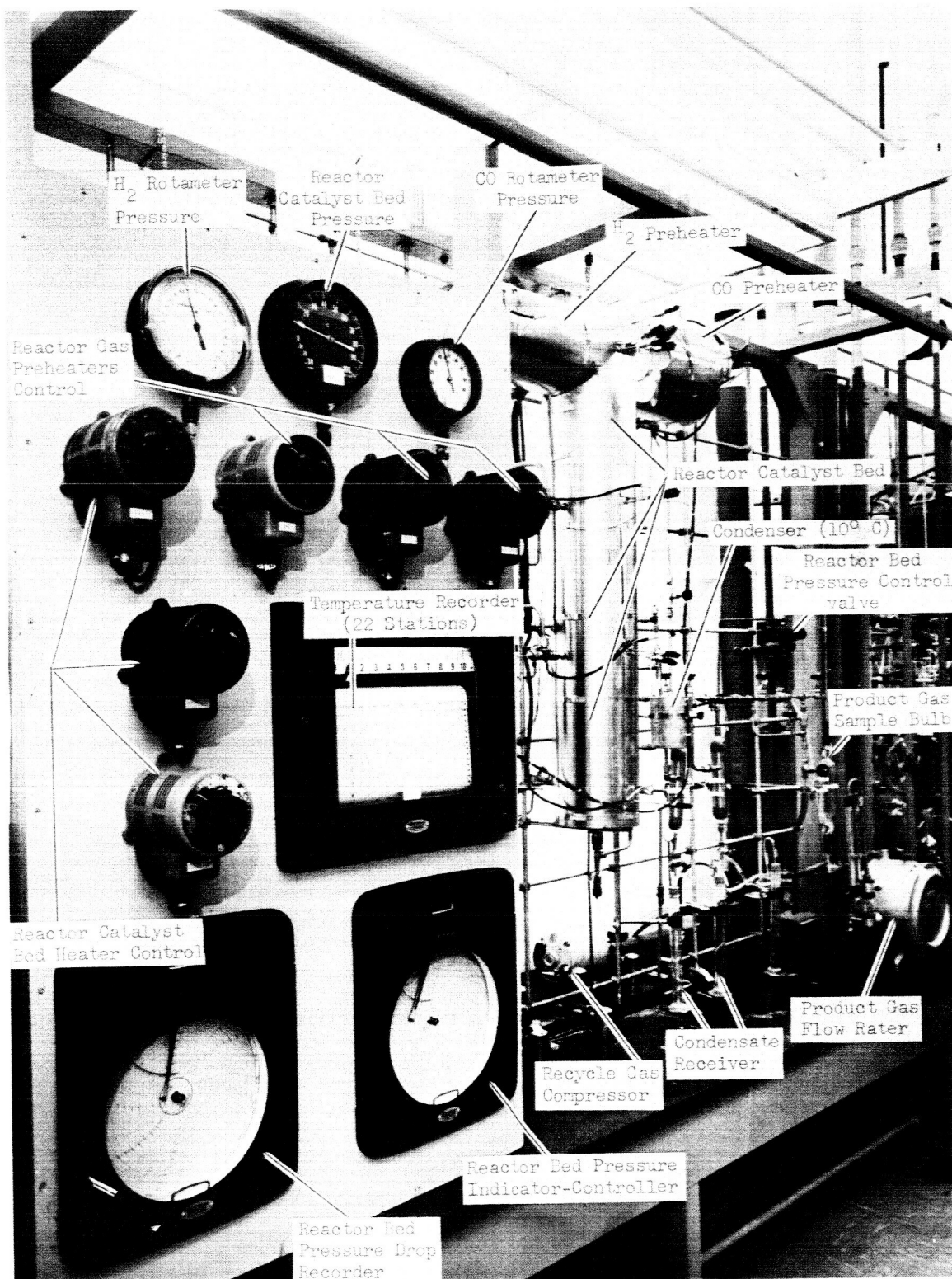


SCHEMATIC FLOW DIAGRAM OF  $H_2$ -CO REACTOR



563-1252

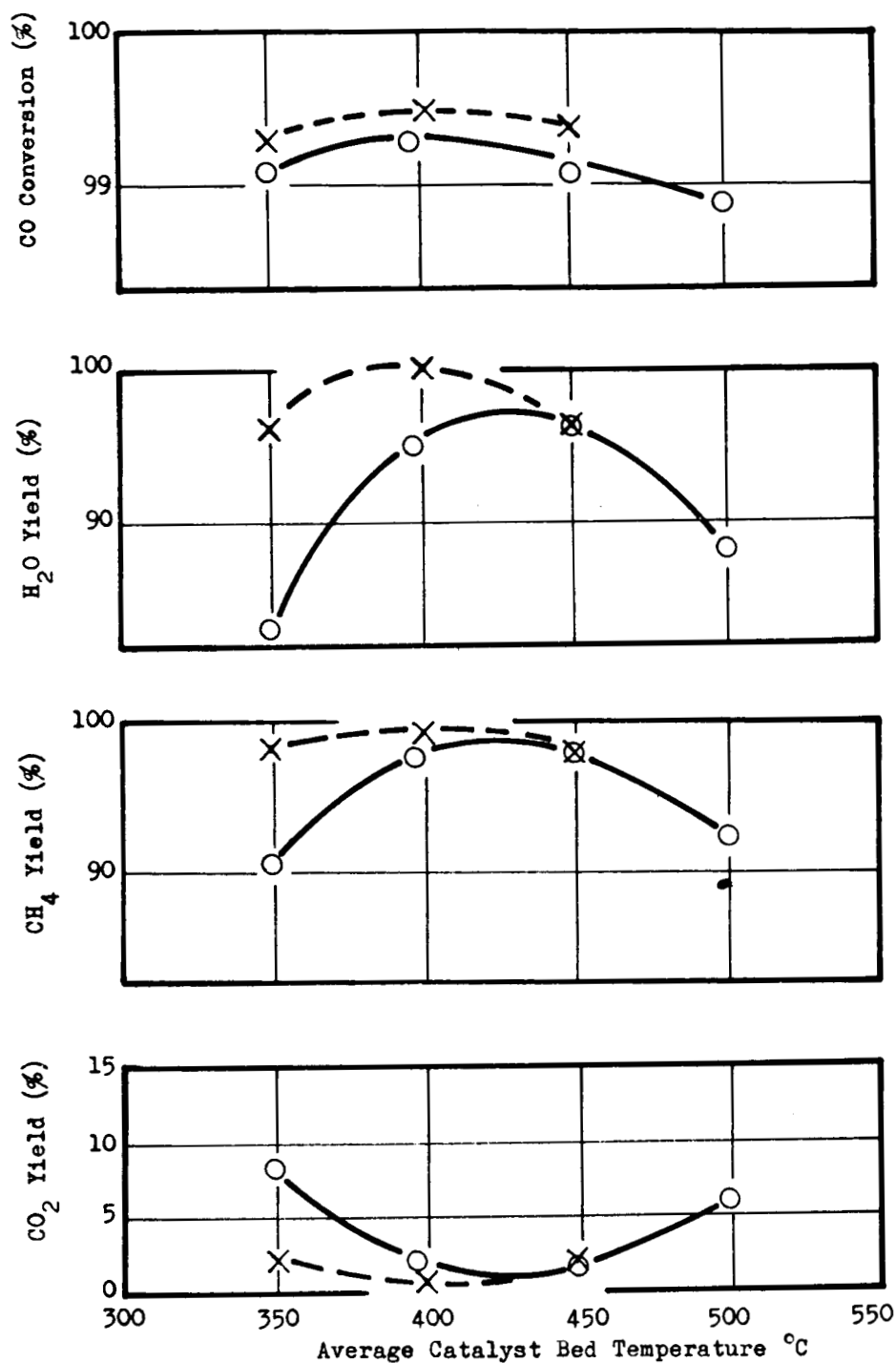
Figure 2 Flow Reactor for Reduction of CO with H<sub>2</sub> During Construction



663-558

Flow Reactor for Reduction of CO with H<sub>2</sub>

Figure 3



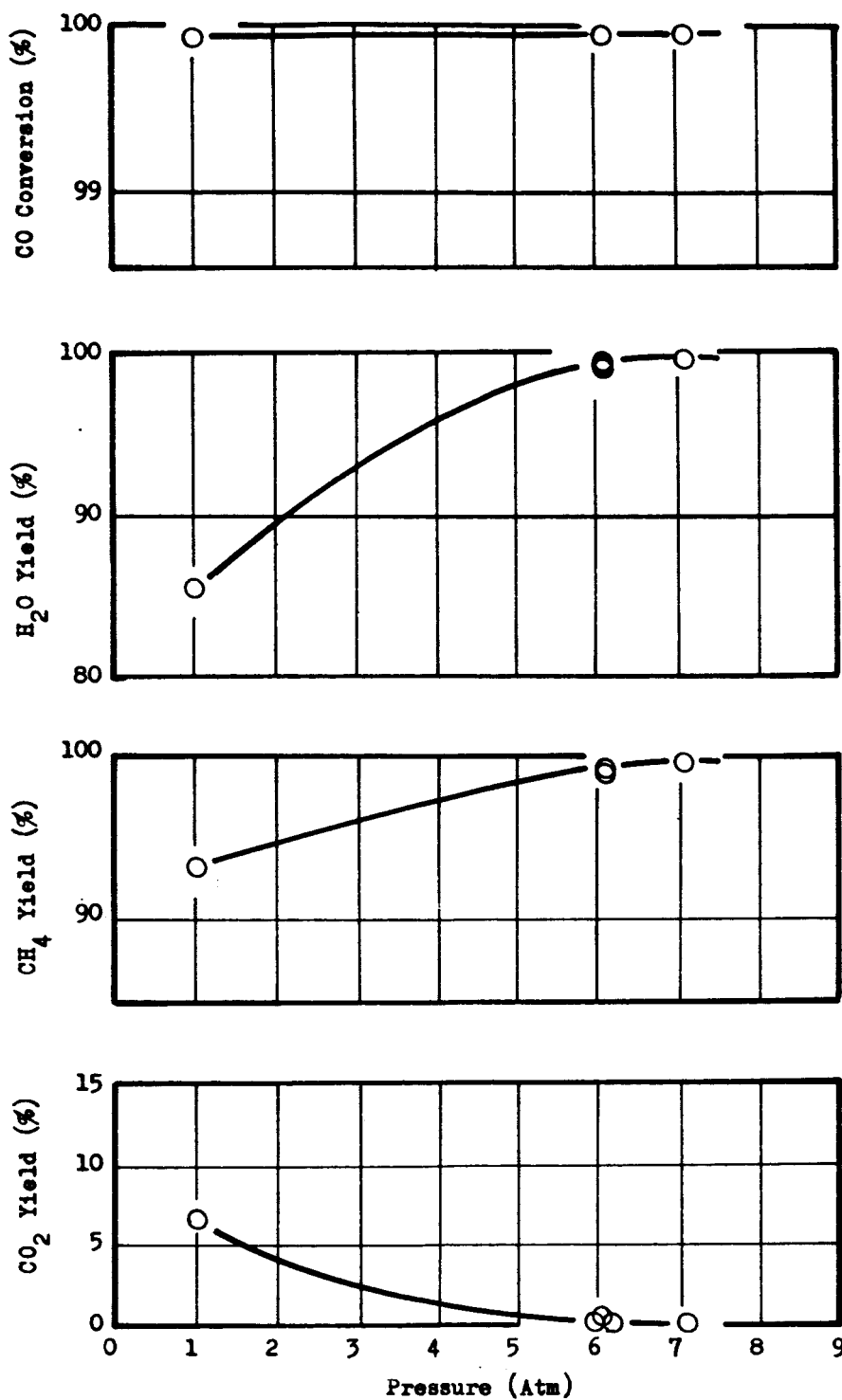
CO CONVERSION AND YIELDS VS TEMPERATURE,  
CATALYST C-0765-1005

4:1 H<sub>2</sub>:CO Ratio; Atmospheric Pressure; 500 Space Velocity

First Catalyst Charge ○ Second Catalyst Charge ×

Figure 4

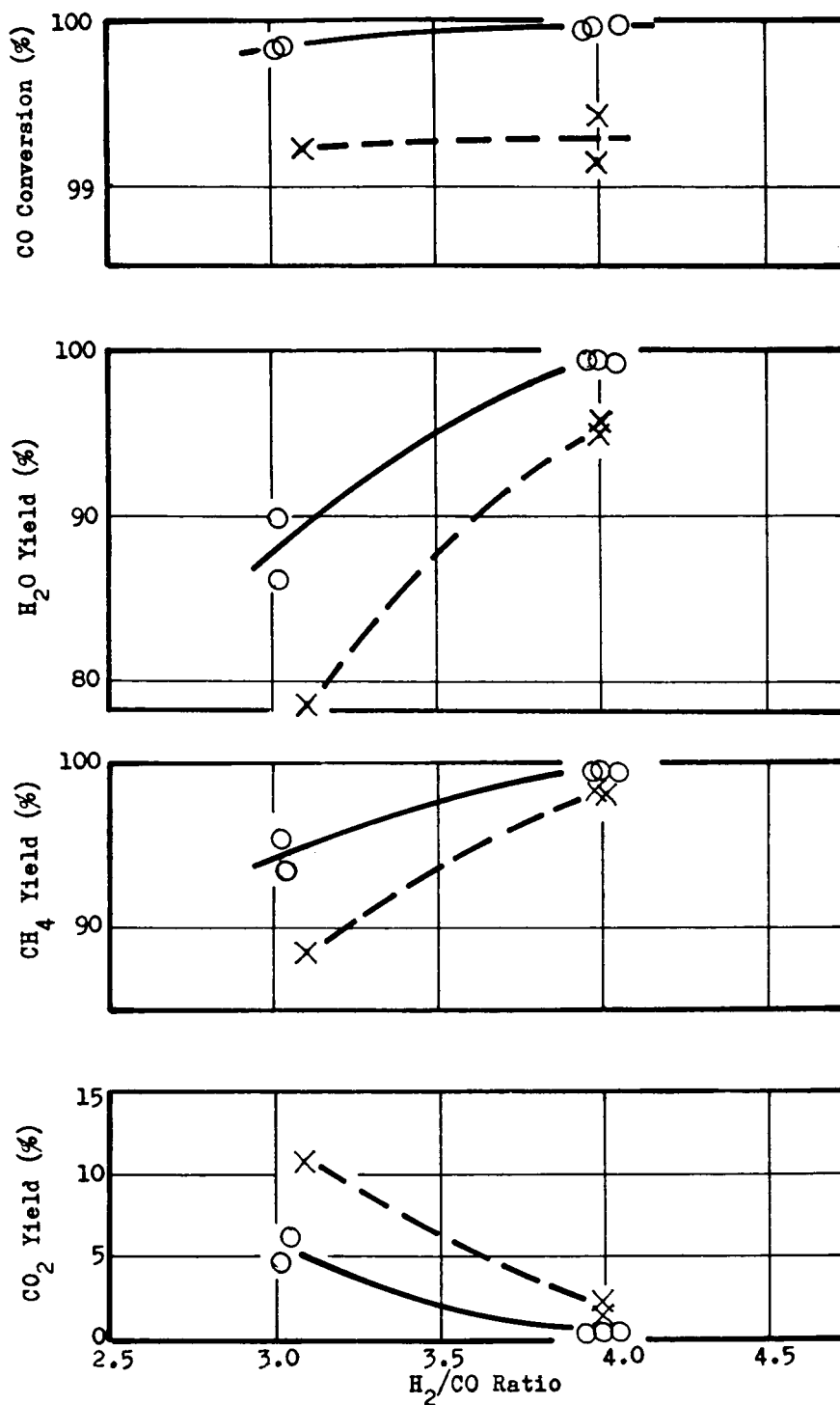




CO CONVERSION AND YIELDS VS CATALYST BED PRESSURE,  
CATALYST C-0765-1005

4:1 H<sub>2</sub>/CO Ratio; 1000 Space Velocity; 450°C

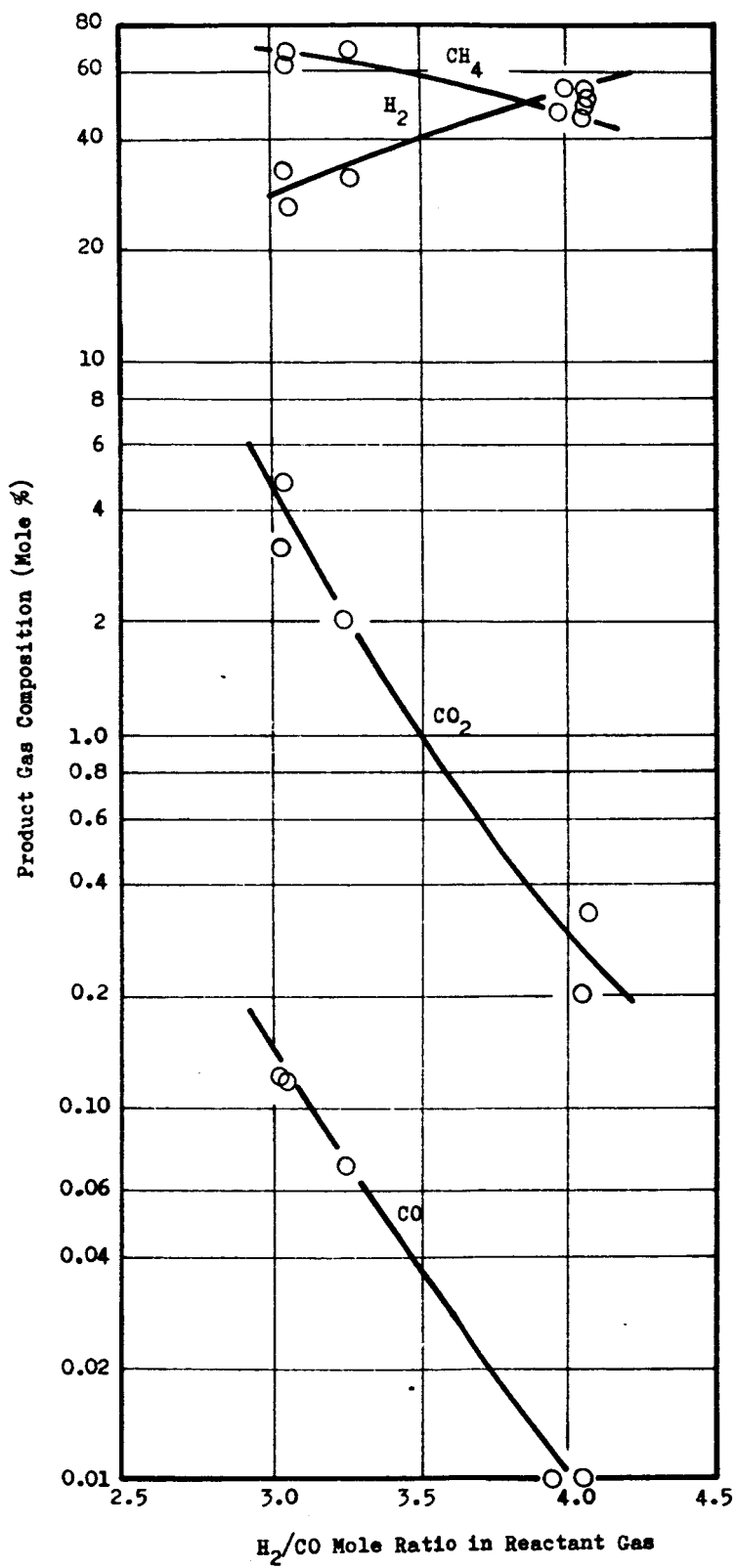
Figure 5



CO CONVERSION AND YIELDS VS H<sub>2</sub>/CO MOLE RATIO,  
CATALYST C-0765-1005

1000 Space Velocity; 450°C; 6.1 Atm ———  
500 Space Velocity; 450°C; 1.0 Atm - - -

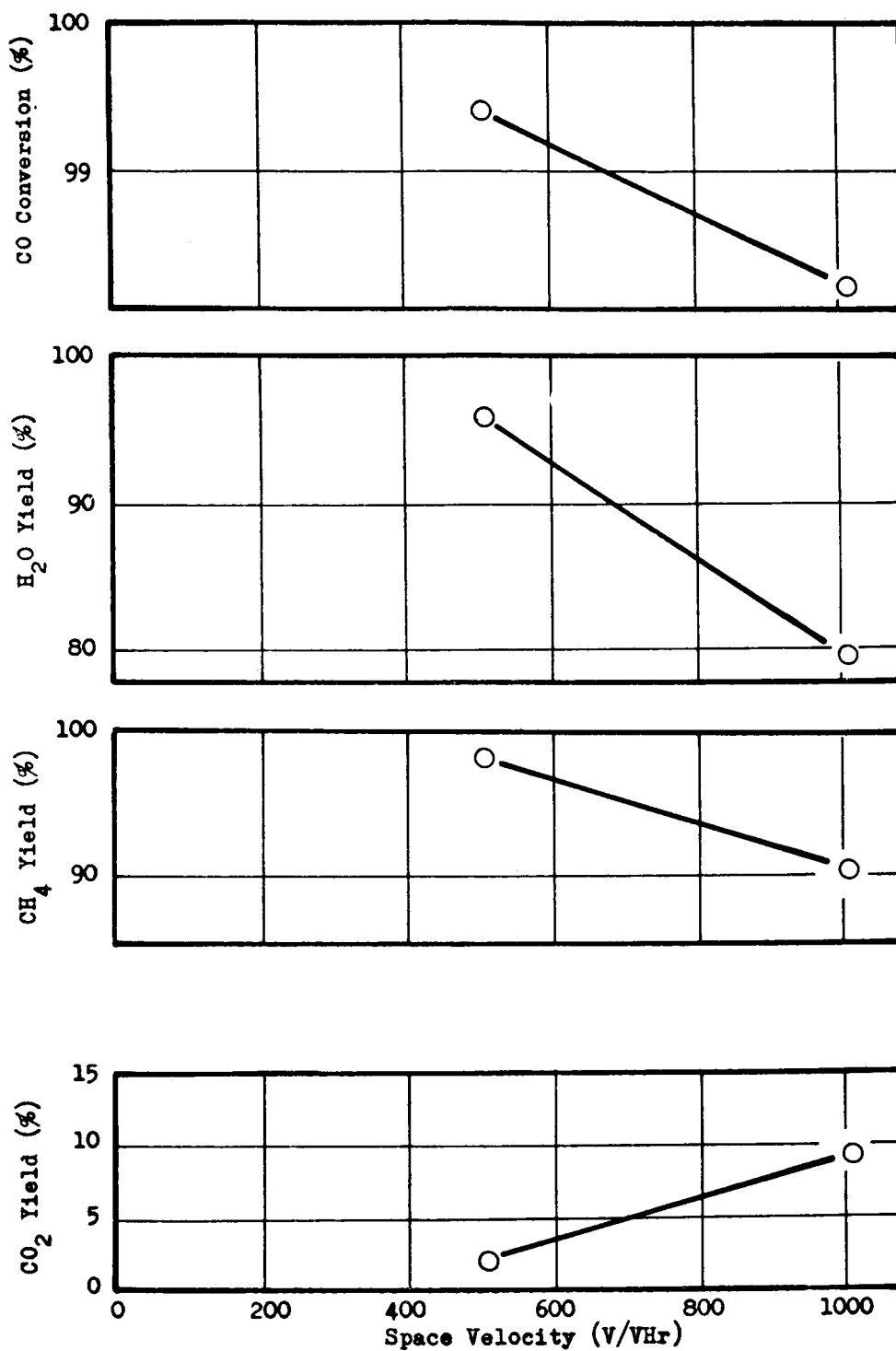
Figure 6



PRODUCT GAS COMPOSITION VS  $H_2/CO$  MOLE RATIO  
CATALYST C-0765-1005

750-1000  $HR^{-1}$  Space Velocity; 450°C; 6.1 Atm

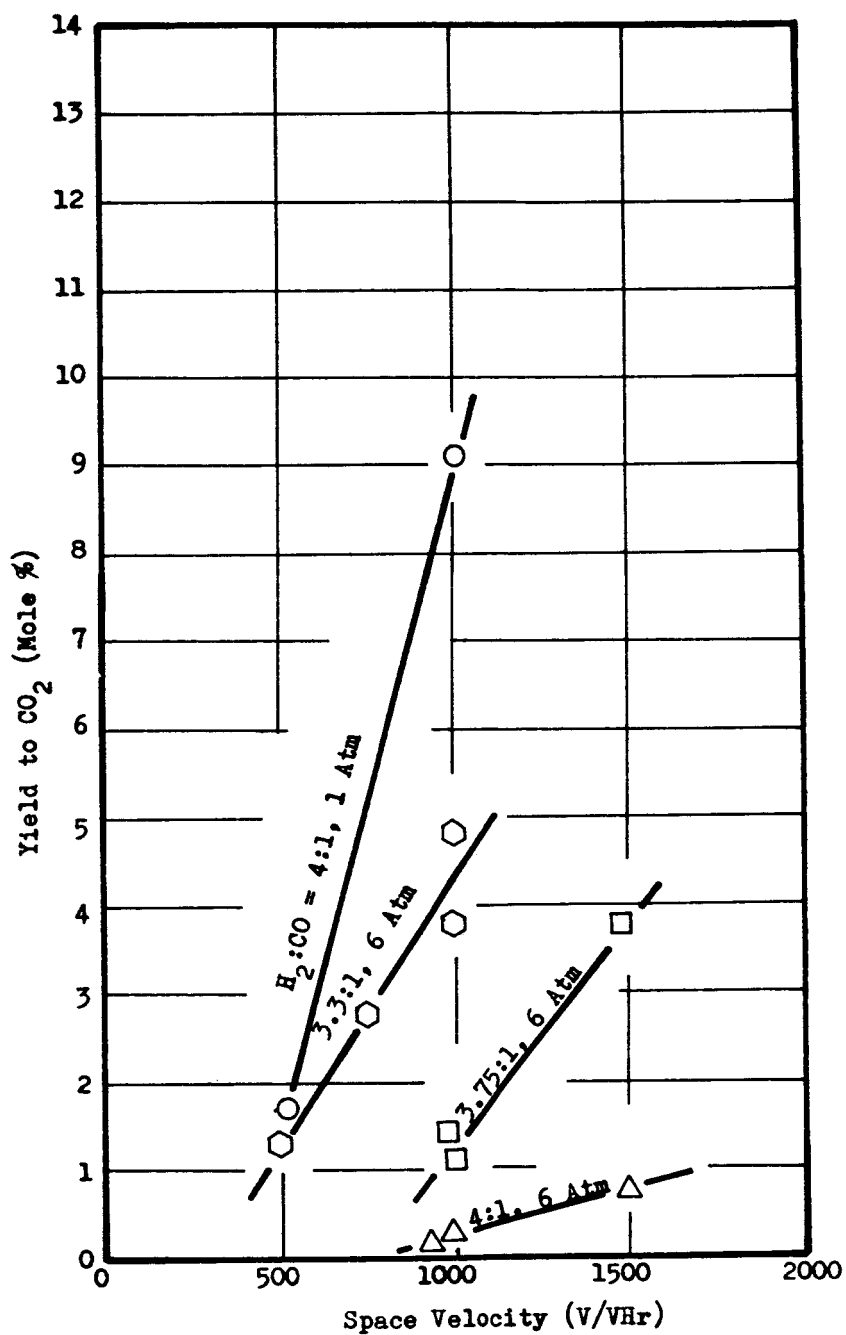
Figure 7



CO CONVERSION AND YIELDS VS SPACE VELOCITY,  
CATALYST C-0765-1005

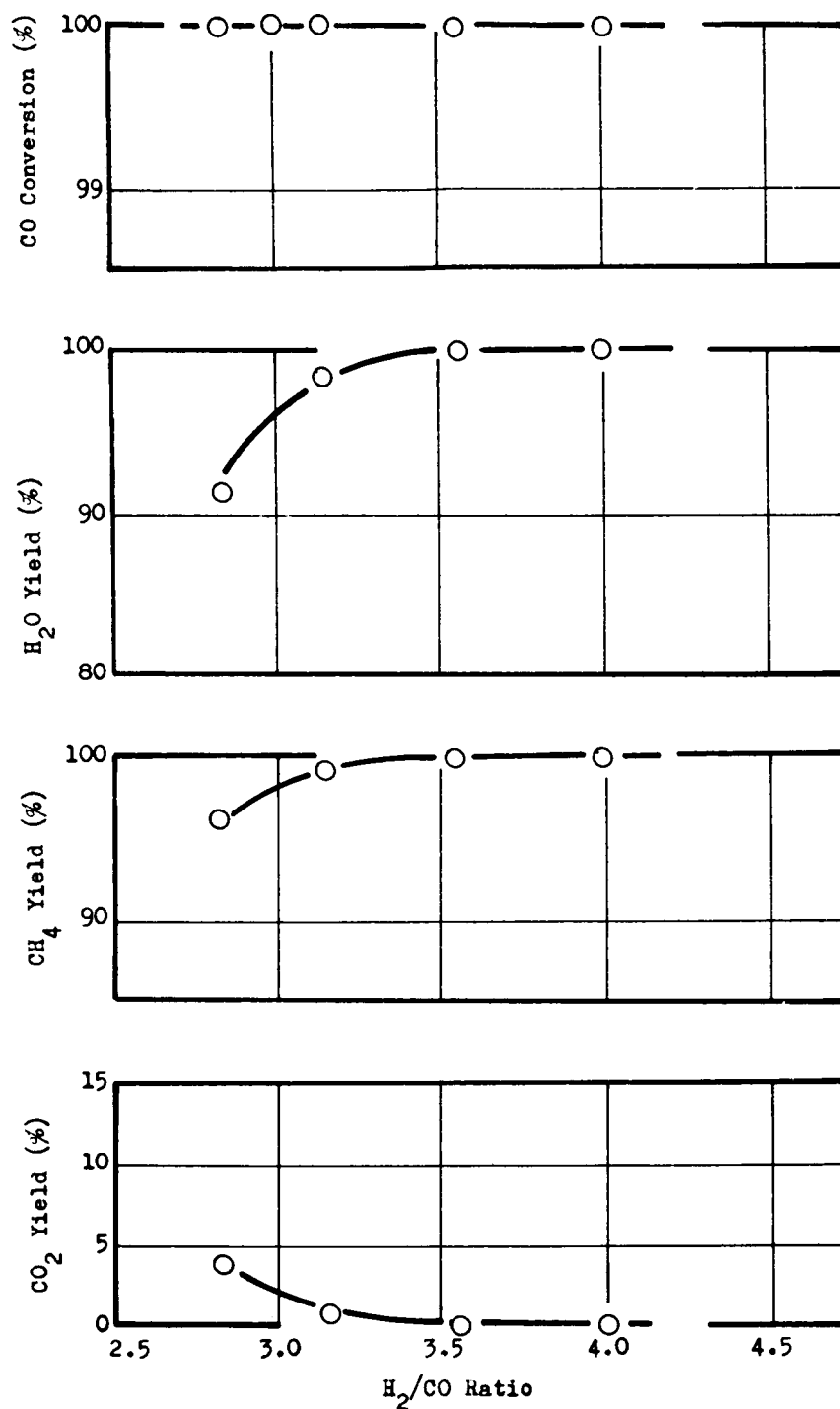
4:1 H<sub>2</sub>/CO Ratio; Atmospheric Pressure; 450°C

Figure 8



YIELD TO CO<sub>2</sub> VS SPACE VELOCITY,  
 CATALYST C-0765-1005  
 450°C Nominal Catalyst Bed Temperature

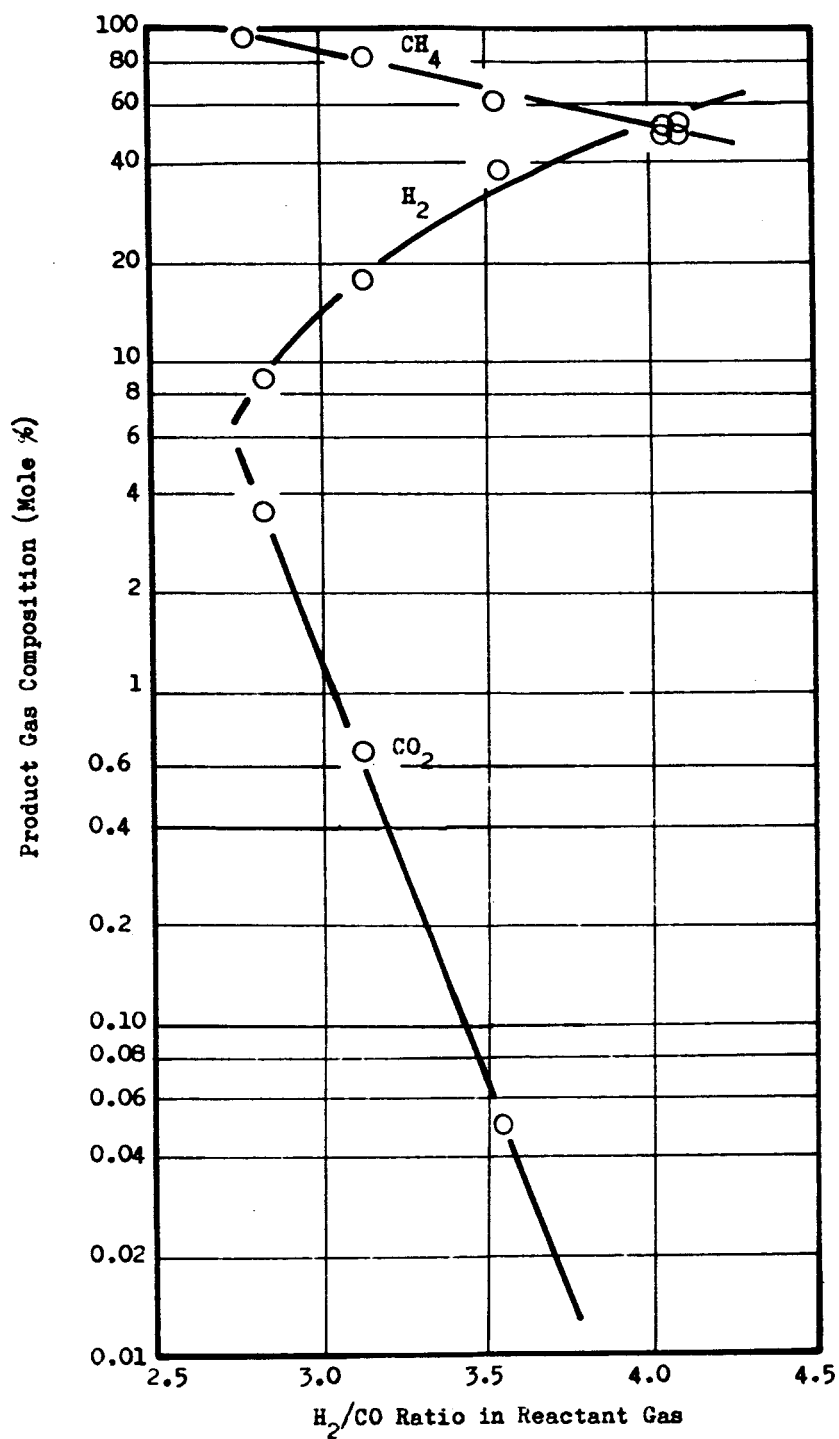
Figure 9



CO CONVERSION AND YIELDS VS  $H_2/CO$  MOLE RATIO,  
CATALYST C-0765-1001

$1000 \text{ hr}^{-1}$  Space Velocity;  $250^\circ\text{C}$ ; 1.0 Atm

Figure 10

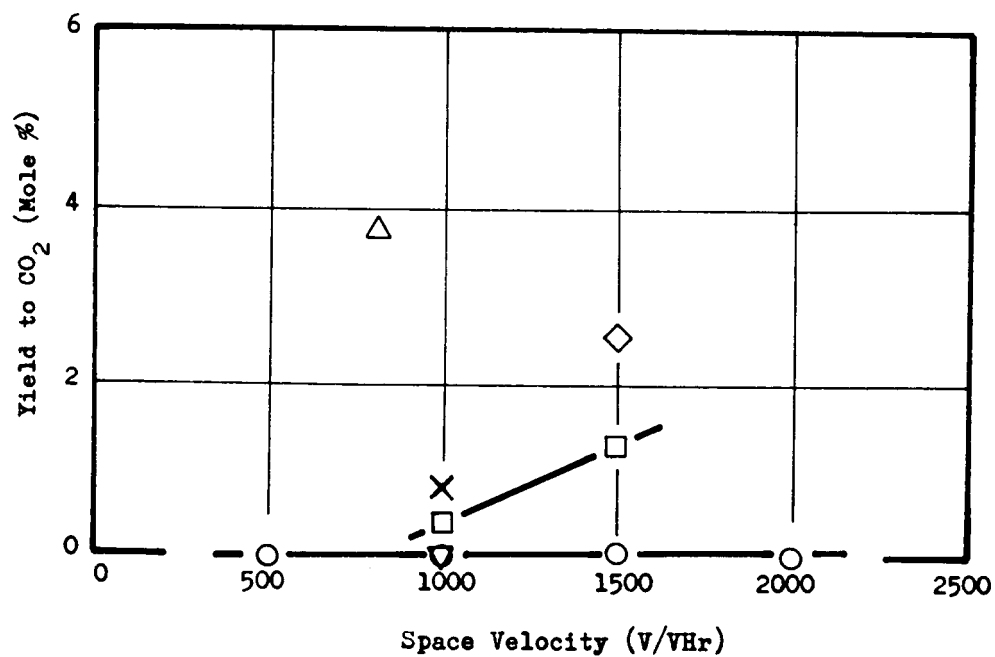


PRODUCT GAS COMPOSITION VS  $\text{H}_2/\text{CO}$  MOLE RATIO,  
CATALYST C-0765-1001

$1000 \text{ hr}^{-1}$  Space Velocity;  $250^\circ\text{C}$ , 1.0 Atm

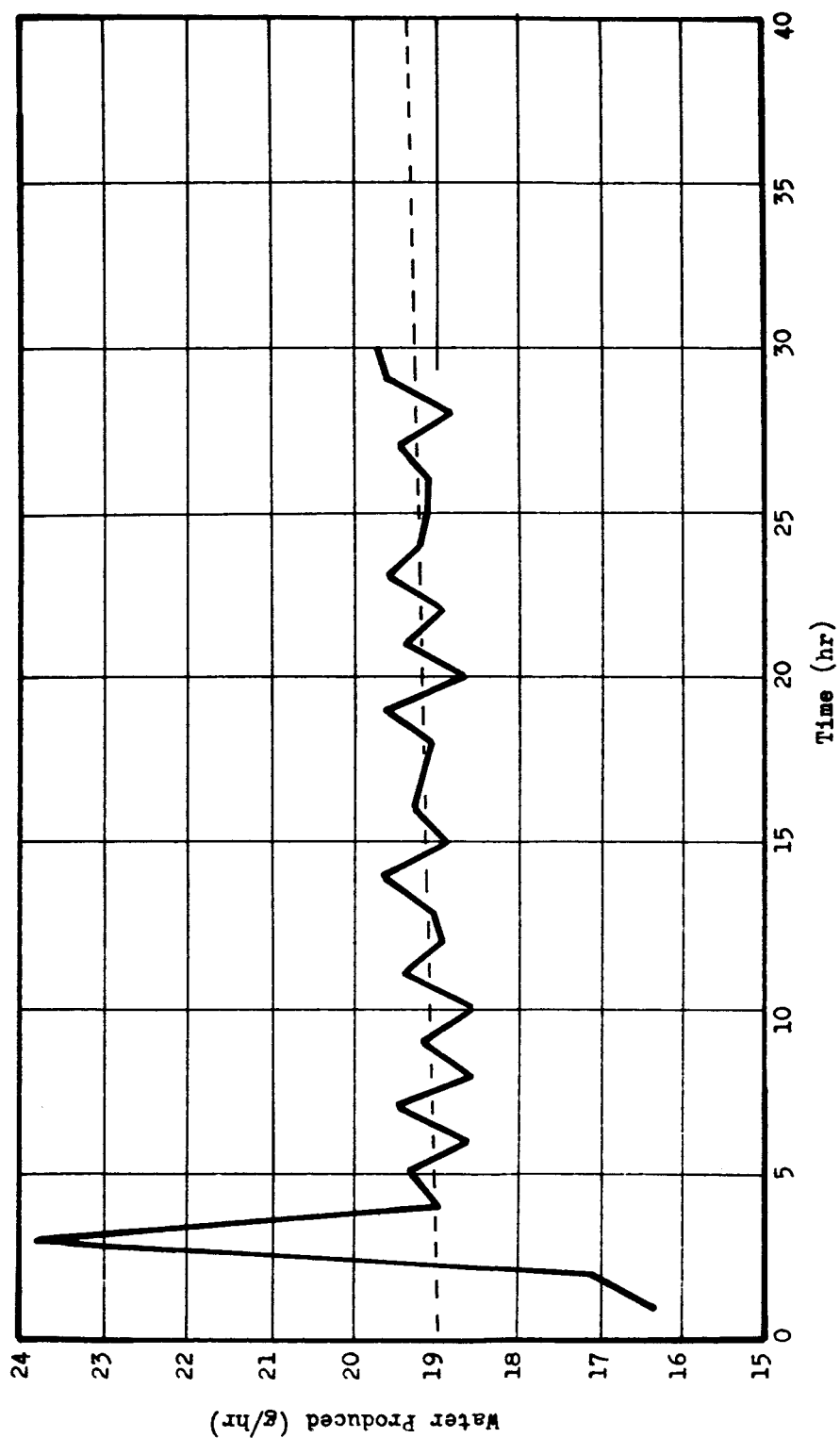
Figure 11

Legend:	$H_2/CO$	Temp. (°C)	Press. (Atm)
○	4.10	250	1.0
▽	3.56	254	1.0
×	3.14	254	1.0
△	2.84	248	1.0
□	3.00	250	6.1
◇	3.02	353	6.1



YIELD TO CO<sub>2</sub> VS SPACE VELOCITY,  
CATALYST C-0765-1001

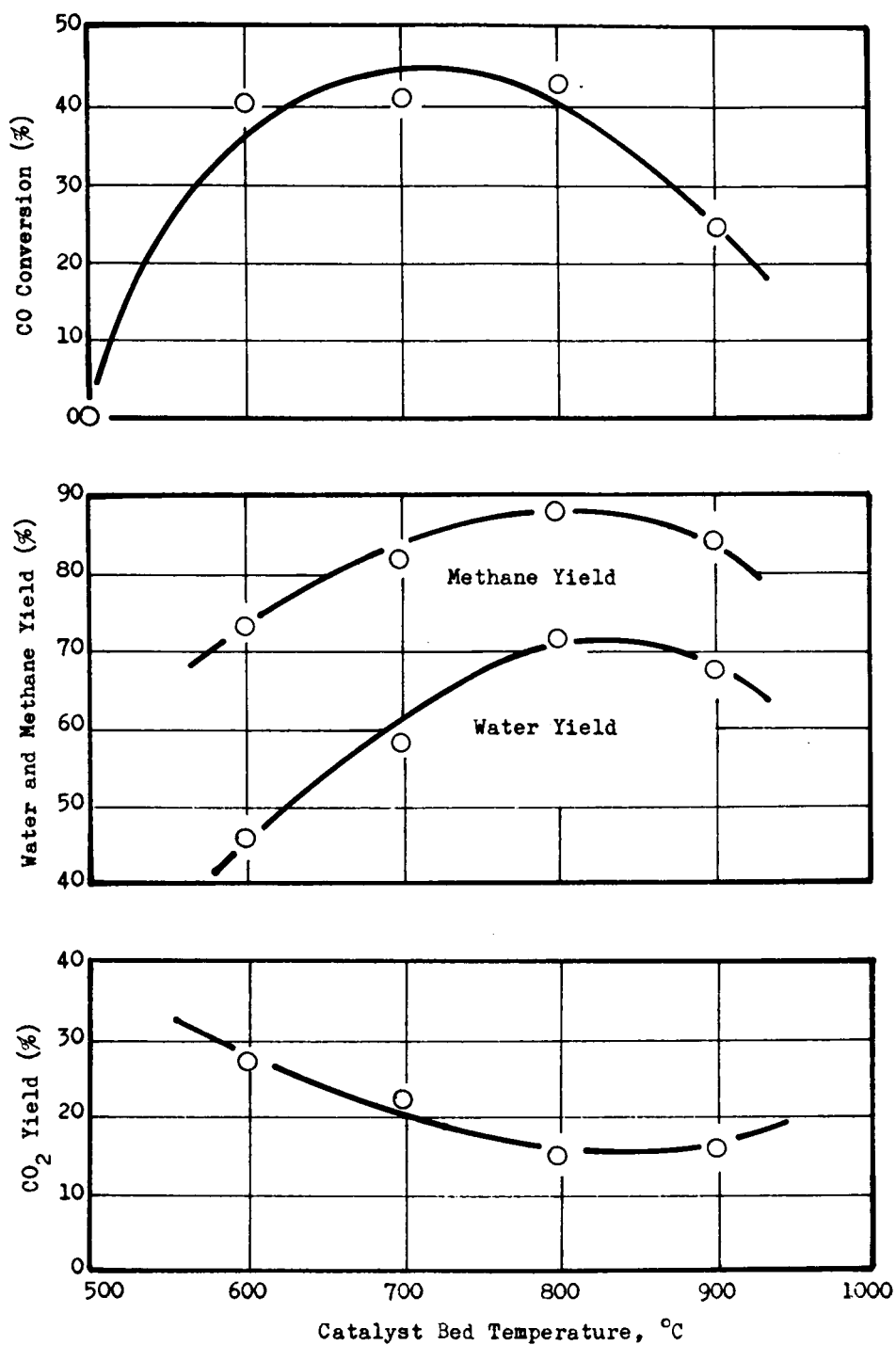




WATER PRODUCTION RATE VS TIME FOR RUN 49,  
CATALYST C-0765-1001

1 atm, 250°C, 4:1 Mole Ratio, 1000 hr<sup>-1</sup> Space Velocity

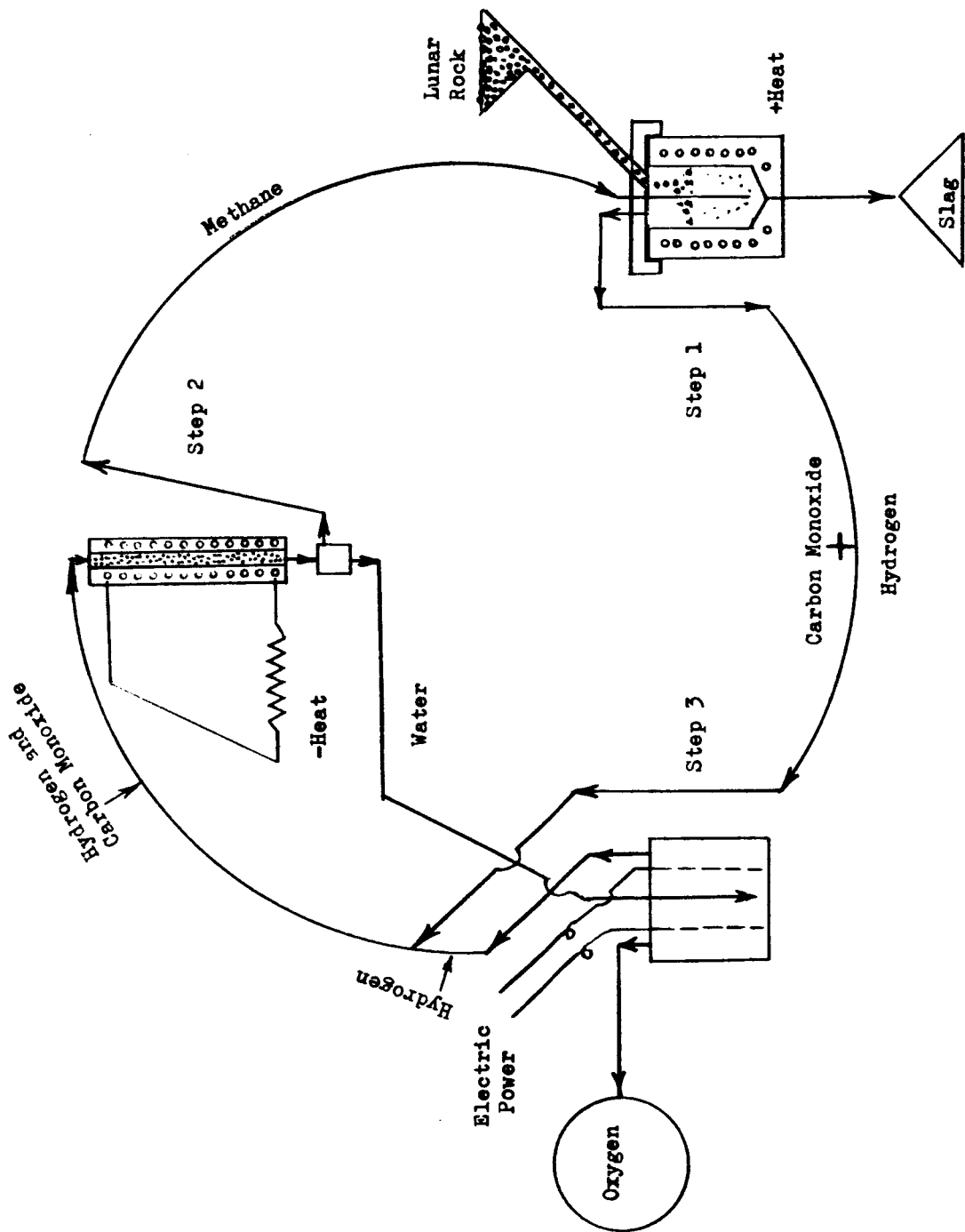
Figure 13



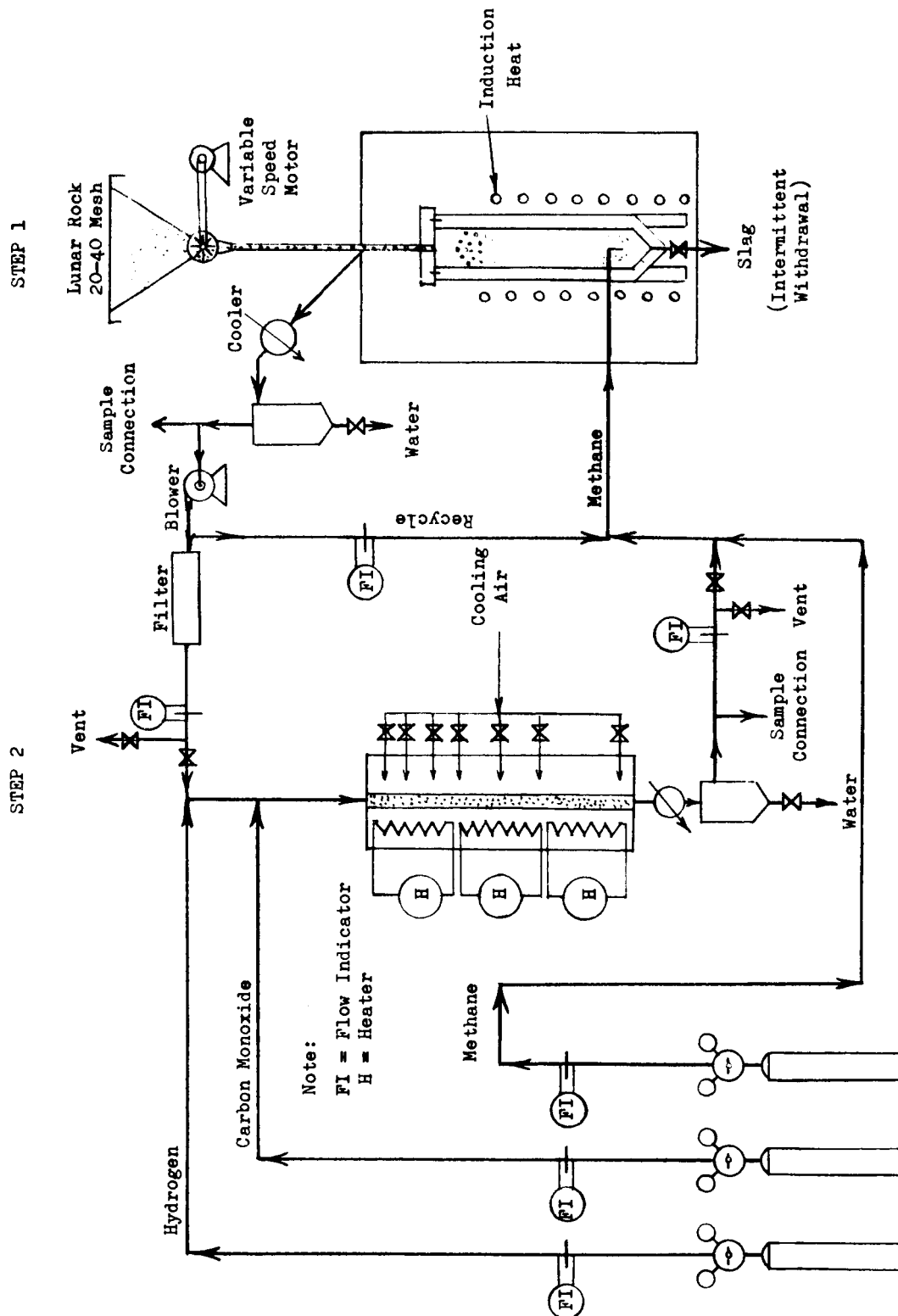
CO CONVERSION AND YIELDS VS CATALYST BED TEMPERATURE,  
BARE TUBE (No Catalyst)

3.7:1 H<sub>2</sub>/CO Mole Ratio; 553 hr<sup>-1</sup> Space Velocity; 6.1 Atm Bed Pressure

Figure 14

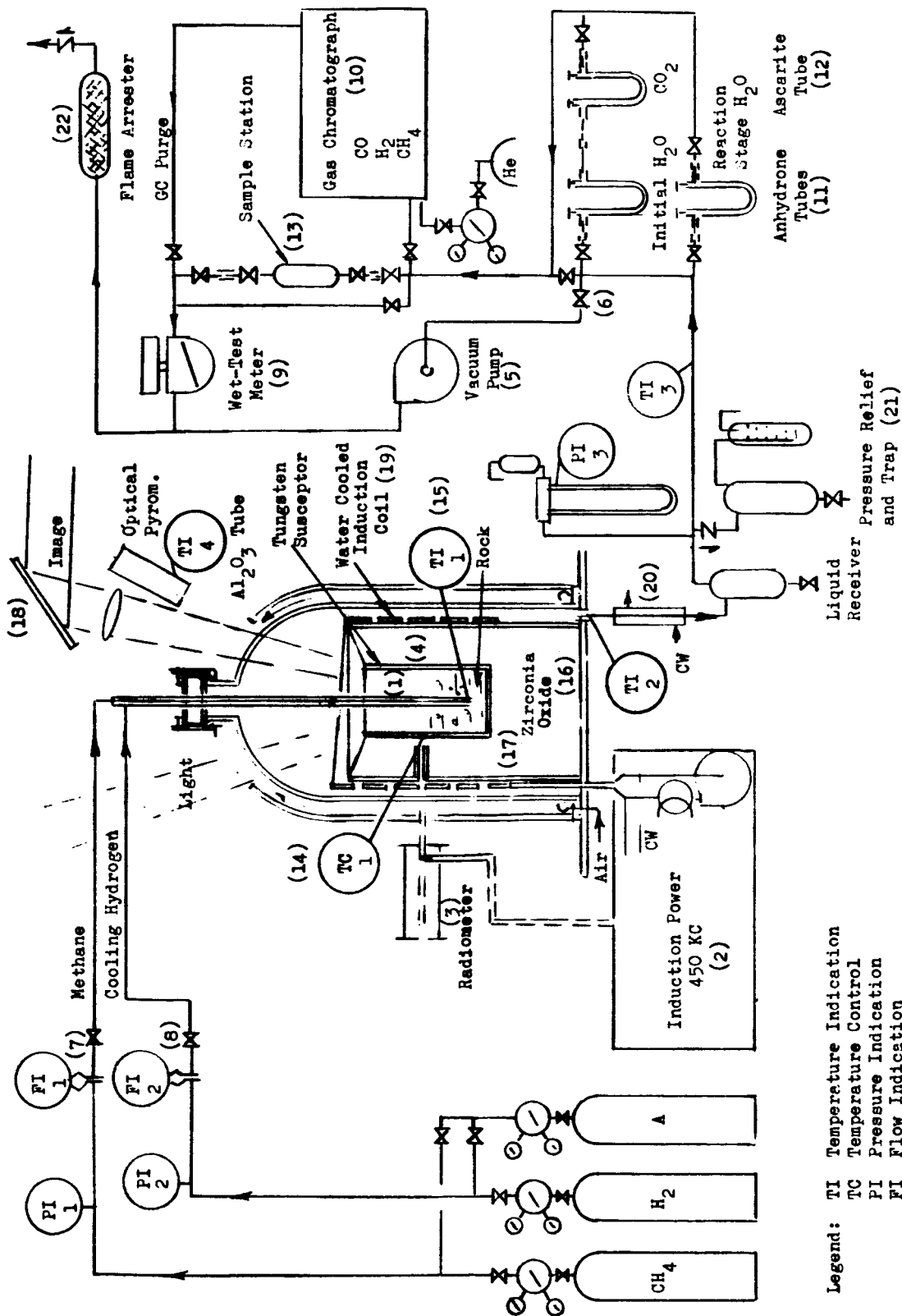


FLOW DIAGRAM FOR  
AEROJET CARBOTHERMAL PROCESS



FLOW DIAGRAM FOR STEPS 1 AND 2  
AEROJET CARBOTHERMAL PROCESS

Figure 16



SCHMATIC FLOW DIAGRAM OF SILICATE REDUCTION FURNACE  
STEP 1. AEROJET CARBOTHERMAL PROCESS